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THE SYNTHESIS AND PROPERTIES OF TERTIARY METHANES*

By FREDERICK CHALLENGER† and DONALD A. PANTONY‡

SUMMARY

A series of tri-*n*-alkylmethanes $(C_nH_{2n+1})_3C.H$ where $n = 3$ to 12 have been prepared from the appropriate Grignard reagent and carbon dioxide, diethyl carbonate, ethyl chloroformate, or other convenient ester. The resulting trialkylcarbinols were dehydrated to the olefins, which were catalytically reduced to the tri-*n*-alkylmethanes. Refractive index, density, surface tension, and dielectric constant were determined, and the molecular refraction, parachor, and electric polarization were calculated.

THE investigation here described is part of a project of the Research Association of British Rubber Manufacturers.

Much work has been carried out in the last few decades on the preparation of pure hydrocarbons for physico-chemical investigations, but very few details have appeared relating to compounds of the type $(C_nH_{2n+1})_3C.H$, where n is greater than four. The tertiary methanes tri-*n*-propyl- to tri-*n*-dodecylmethane have now been prepared in a highly purified state. To ensure that all the alkyl groups of the required tertiary methanes were of the normal structure, all starting materials were carefully fractionated to, at most, a one-degree range of boiling point. Isomers boil at a sufficiently low temperature to be separated by this means, and, provided that no isomerization took place during preparation or purification, the end products may be regarded as pure tri-*n*-alkylmethanes.

Tri-n-alkylmethanes

The most successful method involved (A) the preparation of the tri-*n*-alkylcarbinols by the action of ethyl carbonate [1] or ethyl chloroformate [2] on three equivalents of *n*-alkyl magnesium bromide, followed by dehydration [3, 4] and subsequent catalytic hydrogenation.[5, 6] Overall yields were good, even for the higher members of the series, provided that certain precautions were taken throughout all stages.

Other methods that were employed were: (B) the action of dry carbon dioxide [3] or (C) carboxylic esters [7] RCOOEt on *n*-alkyl magnesium bromides RMgBr to prepare the carbinols, $R_3C.OH$; and also (D), the selective action of acetylenic magnesium bromides on ketones.[8] The first method, although satisfactory for the lowest members, was not so for those of higher carbon content, and the second method proved less suitable for the hydrocarbons under investigation, although it may be a valuable synthetic method for very long-chain compounds.

Dehydration was carried out either with oxalic acid [3] or catalytically with iodine.[4] The second reagent proved most convenient in that dehydration and distillation could be carried out in one operation. For hydrogenation of the resulting olefin a catalyst of palladium on a charcoal carrier at approximately atmospheric pressure, or Adams platinum oxide catalyst under high pressure, were used.

Purity of the Products

At all stages in the preparation the various products were fractionally distilled through a high-efficiency column packed with Fenske helices. In general, reduced pressure was used, and even with pressures of less than 1 mm the column proved to be efficient. However, even under this pressure the boiling points of the highest members of the series were in the region of 200° C and the boiler was kept at a temperature up to 300° C. At this temperature "cracking" [9] and oxidation caused by air entering through the capillary leak were noticeable, in that the products were yellow in colour and anomalous physical constants were obtained for the saturated hydrocarbons.

In these cases molecular distillation [10] and chromatographic absorption [11] were employed with success in the final purification. Figures obtained on analysis proved to be useless as a control of purity, since neighbouring homologues and parent olefins give figures which are analytically indistinguishable. Even the yellow products obtained on a first fractional distillation gave on analysis figures practically identical with the calculated ones. Several physical methods of control were used, including determination of the parachor,[12] molecular refraction, and molecular polarization (calculated from the dielectric constant).

The parachor proved a useful constant, in that it identified the products but was insensitive to impurities. The same objection applied to molecular refraction, although to a lesser extent. The most sensitive control was found in the measurement of the static dielectric constant [13] of the paraffins, this constant being brought to a minimum value by repeated purification. Fortunately, the dielectric constants of such possible impurities as ketones, olefins, alkyl halides, etc, are much higher than those of the hydrocarbons, and traces elevate the values considerably. Alternatively, the values of the exaltation of molecular polarization and molecular refraction were equated, within experimental error. It can be

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shown [14] theoretically that these two exaltations, due to the tertiary carbon grouping in the molecule, should be equal. The use of the molecular exaltations is limited by the wide differences in the numerical values of the molecular weights of the compounds. This introduces a serious error for the higher members which can, however, be easily overcome by using the corresponding exaltations of the volume refraction and polarization which are also equal to one another. These theoretical considerations are dealt with in greater detail in the succeeding communication.

It should be noted that the constancy of the boiling points of the hydrocarbons has no significance, since small quantities of low-boiling decomposition products would distil without altering the thermometer reading, and because the pressure in a high vacuum distillation unit fluctuates considerably, depending on the "flooding" of the column, the "vapour pad" over the boiling liquid, and the pressure drop from the thermometer at the top to the boiler at the bottom of the column, all of which may vary. Even the pressure reading was not a true one, since the manometer was situated close to the pump. Clearly, then, boiling point constants of the products are only "constants" for a particular system, and are not necessarily reproducible to within several degrees.

Several compounds described in this paper appear to be new. These include tri-*n*-amyl-, tri-*n*-hexyl-, tri-*n*-heptyl-, tri-*n*-octyl-, and tri-*n*-decyl-carbinols, the corresponding alkenes and also the alkanes tri-*n*-amyl-, tri-*n*-hexyl-, tri-*n*-heptyl-, tri-*n*-undecyl-, and tri-*n*-dodecyl-methanes.

EXPERIMENTAL

Starting Materials for Preparation of Tri-n-alkylmethanes

Alkyl bromides were made from the corresponding alcohol either by the action of 48 per cent hydrobromic acid and sulphuric acid [15] or, in the case of involatile bromides, by the action of dry hydrogen bromide on the dry alcohol at 120° C.[16] Yields were always 80 to 95 per cent of theoretical.

When alcohols were not available, *i.e.*, those with an odd number of carbon atoms, these were made from other alcohols or by reduction of a suitable ethyl ester. These methods involved the action of dry ethylene oxide [17] or of formaldehyde,[18, 19] on an alkyl magnesium bromide, or the Bouveault–Blanc reduction of an ester.[20]

$$2RMgBr + 2CH_2{-}CH_2 \;(\text{O bridge}) \longrightarrow (R.CH_2.CH_2O)_2Mg + MgBr_2 \quad . \quad . \quad (i)$$

$$\xrightarrow{H_2O} 2R.CH_2.CH_2OH$$

$$RMgBr + H.CHO \longrightarrow R.CH_2.OMgBr \xrightarrow{H_2O} R.CH_2.OH \quad . \quad (ii)$$

$$R.COOC_2H_5 \xrightarrow{Na/EtOH} R.CH_2OH \quad . \quad (iii)$$

The formaldehyde method proved most useful in that an odd-numbered alcohol was obtained from an even-numbered one.

Preparation of n-*undecyl alcohol.* 36 g of carefully dried paraformaldehyde were thermally decomposed and the vapour passed through very clean delivery tubes into a Grignard reagent, made from 29·5 g of magnesium turnings dissolved in 260 g of *n*-decyl bromide in 900 ml of sodium-dried ether, cooled to −60° C in an acetone–carbon dioxide freezing mixture. Stirring was continuous, and when all the formaldehyde had been added the mixture was warmed on the steam bath for 2 hr. Decomposition was carried out with 100 g of ammonium chloride and 600 g of ice. Isolation of the *n*-undecyl alcohol gave 160 g (87 per cent) of product, b.p. 135° C at 19 mm. The extreme cleanliness of the 8-mm bore delivery tube prevented polymerization of the formaldehyde, and the cooling of the Grignard reagent prevented loss of formaldehyde by polymerization or escape from the reaction mixture.

Preparation of n-*nonyl bromide and di-*n-*nonyl formal.* The reaction was repeated, using 43·5 g of magnesium dissolved in 348 g of *n*-octyl bromide in 1500 ml of ether and 75 g of paraformaldehyde (*i.e.*, a 20-g excess). A yield of 105 g (*i.e.*, 41 per cent) of *n*-nonyl bromide, b.p. 105° C at 15 mm was obtained from the resulting *n*-nonyl alcohol. In addition, 125 g of another product, b.p. 153° to 154° C at 0·8 mm, m.p. 7° to 8° C, were obtained. Subsequent analysis of this oil showed it to be slightly impure di-*n*-nonyl formal, produced by the reaction :

$$\begin{matrix} C_8H_{17}.CH_2.O\boxed{MgBr} \\ C_8H_{17}.CH_2.O\boxed{MgBr} \end{matrix} + O{=}C\begin{matrix}H\\H\end{matrix} \longrightarrow \begin{matrix} C_8H_{17}.CH_2O \\ C_8H_{17}.CH_2O \end{matrix}\!\!>\!C\!<\!\begin{matrix}H\\H\end{matrix} \quad . \quad (iv)$$

The product was hydrolysed by boiling with a large excess of 48 per cent hydrogen bromide solution for 5 hr, and the oily upper layer isolated by distillation of the reaction mixture. An amount of 100 g of the formal gave 135 g of *n*-nonyl bromide, b.p. 100° to 101° C at 16 mm, when refluxed with 500 ml of hydrobromic acid. The bromide was identified by the formation of decoicanilide, $C_9H_{19}CONHC_6H_5$, m.p. 68° to 69° C, by the action of phenyl *iso*cyanate on the corresponding Grignard reagent,[21] and formaldehyde was shown to be present in the aqueous layer of the distillate by formation of its 2 : 4-dinitrophenylhydrazone, m.p. 165° to 166° C, and dimedone compound, m.p. 188·5° C, but absent in the free state in the by-product.

The preparation of nonyl bromide in a yield so

high as 98 per cent makes this method a very attractive one for the preparation of the next higher bromide in a homologous series without intermediate formation of the alcohol. Sufficient excess of paraformaldehyde might be used to ensure complete conversion of the Grignard reagent to the formal.

Similar results were obtained with the action of excess formaldehyde on *n*-hexyl magnesium bromide, the di-*n*-heptyl formal having a b.p. of 160° to 161° C at 18 mm.

Grignard Reagents

The *n*-alkyl magnesium bromides were prepared in a uniform manner using magnesium turnings as massive as possible, so that oxide and moisture layers were minimized. These layers are known to catalyse the Wurtz–Fittig reaction.[22]

$$RMgBr + RBr \longrightarrow RR + MgBr_2 \quad . \quad (v)$$

In addition, it was found that high local temperatures and concentration enhanced this reaction, particularly for higher homologues. Hence very great dilutions—up to 1 l per mol of alkyl bromide—were employed, with a corresponding prolongation of reaction time. As far as possible, the ether solutions of the Grignard reagent were gently refluxed to prevent air from coming in contact with the reagent and the subsequent oxidation

$$RMgBr + [O] \longrightarrow R.OMgBr \longrightarrow R.OH \text{ [23]} \quad (vi)$$

and to prevent formation of the alcohol on final hydrolysis from taking place. Evidence of this reaction was found in cases where such precautions were not taken. Where it was impossible to maintain the ether at a gentle boil, dry nitrogen was introduced through the stirrer shaft.

Di-*n*-butyl ether, carefully purified, was used in some cases.[24] It was found to be unsatisfactory as a solvent, since, although higher temperatures could be attained and the reactions accelerated, the decomposition [25]

$$R.CH_2.CH_2.MgBr \longrightarrow R.CH{=}CH_2 + HMgBr \quad (vii)$$

was facilitated, and evidence of the presence of olefins was found in some reactions.

Preparation of the Carbinols R_3COH

(a) *Use of carbon dioxide.*[3] A measured volume of dry carbon dioxide was introduced in a very slow stream below the surface of vigorously stirred boiling ethereal solutions of the Grignard reagents prepared from *n*-propyl, *n*-butyl, and *n*-amyl bromides. After 12 hr of refluxing and stirring the reaction mixtures were decomposed by dilute sulphuric acid (25 per cent) and ice. Yields of 43, 41, and 39 per cent respectively were obtained after isolating the carbinols by washing with water, 10 per cent aqueous sodium carbonate, water, and then drying over anhydrous sodium sulphate, followed by fractional distillation under reduced pressure. Boiling points: tri-*n*-propylcarbinol, 91° to 92° C at 17 mm; tri-*n*-butylcarbinol, 126° to 127° C at 15 mm; tri-*n*-amylcarbinol, 165° to 167° C at 20 mm.

Considerable quantities of unidentified low-boiling products were obtained in all cases.

(b) *Corresponding ester method.*[7] Tri-*n*-propyl and tri-*n*-amylcarbinols were prepared in 68 and 57 per cent yields, respectively, by adding ether solutions of ethyl butyrate and ethyl caproate to two equivalents of *n*-propyl and *n*-amyl magnesium bromides respectively, and working up the reaction mixtures as described in (*a*). Ammonium chloride was used as the decomposition agent in these cases, instead of dilute sulphuric acid, to minimize possible dehydration of the resulting carbinols. Smaller quantities of unidentified low-boiling products were obtained, and the highest fractions were found to be the desired carbinols: b.p. of tri-*n*-propylcarbinol, 90° to 91° C at 16 mm; tri-*n*-amylcarbinol 154° to 155° C at 11 mm.

(c) *Ethyl carbonate method.*[1] Ether solutions of ethyl carbonate were added to three equivalents of the Grignard reagents prepared from *n*-propyl, *n*-butyl, *n*-hexyl, *n*-heptyl, *n*-octyl, *n*-nonyl, *n*-decyl, *n*-undecyl, and *n*-dodecyl bromides, contained in a suitably sized flask, fitted with a three-necked adapter carrying a dropping funnel, mercury sealed chain stirrer, and double-surface reflux condenser. Addition of the ethyl carbonate solution (1 vol in 3 vol of ether) required up to 4 hr per mol of ethyl carbonate for the higher members of the series, and the reaction was completed by refluxing and stirring for a further 12 to 20 hr.

Decomposition was carried out by pouring on to a mixture of excess ammonium chloride and ice, and, on warming to room temperature, extracting the aqueous layer with ether. Isolation was completed by thorough washing of the combined organic layers with water, drying over anhydrous sodium sulphate for at least 24 hr, removing the ether, and finally distilling the residual oil under reduced pressure.

In most cases the carbinol was isolated, but with certain carbinols dehydration took place during distillation, either thermally or catalytically, due to traces of impurities presumably introduced during the preparation or isolation. In these cases the next stage—viz. full dehydration—was completed in the distillation apparatus. In actual practice it appeared that in no case was the carbinol absolutely pure, since some dehydration always took place during distillation, as evidenced by physical measurements carried out with the acetylenic carbinol (see p. 40) and by decolorization of bromine and alkaline permanganate.

Very rigorous precautions were taken against introduction of air and moisture in one preparation of tri-*n*-decylcarbinol. In this experiment the final yield was hardly affected, and some didecyl was isolated. Hence normal Grignard conditions were used in all other cases.

Yields decreased steadily as the molecular weight of the carbinol increased, but were never less than 40 per cent. In all cases low-boiling products were

obtained, which gave some insight into the mechanism of the reaction.

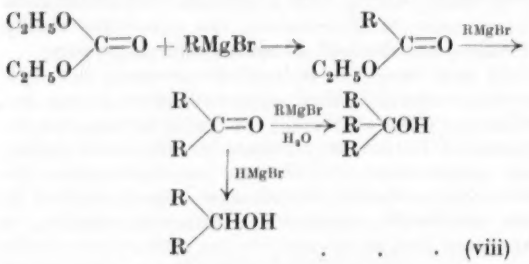
In all cases where the alkyl group contained more than seven carbon atoms the R.R hydrocarbon, obtained as in reaction (v), was isolated as waxy lustrous scales of sharp melting point, after crystallization from a methyl alcohol–ether mixture in a refrigerator. *n*-Hexadecane, $C_{16}H_{34}$, m.p. 22° to 23° C; *n*-eicosane, $C_{20}H_{42}$, m.p. 35·5° to 36·5° C; *n*-docosane, $C_{22}H_{46}$, m.p. 43° to 44° C, and *n*-tetracosane, $C_{24}H_{50}$, m.p. 53° to 54° C, were obtained in this manner.

Ethyl valerate and ethyl caprylate were identified in the products from the reactions of *n*-butyl and *n*-heptyl magnesium bromides on ethyl carbonate respectively. Hydrolysis yielded the acids characterized as the anilides, m.p. 63° C and 53·5° to 54·5° C. The literature records m.p. 63° C and 55° C.

Di-*n*-octyl and di-*n*-nonyl ketones were isolated from the experiments where the corresponding Grignard reagent was employed and identified. Di-*n*-octyl ketone: m.p. 51·5° to 52·5° C; *p*-nitrophenylhydrazone, m.p. 55° C (the literature recording m.p. 53° and 54° C). Di-*n*-nonyl ketone, m.p. 57° to 58° C (the literature recording m.p. 58° C).

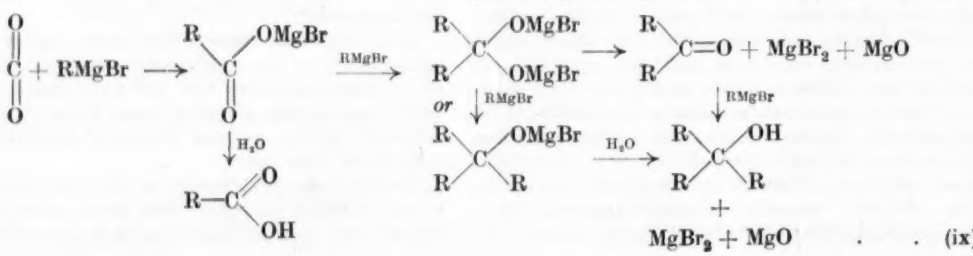
The isolation of di-*n*-undecylcarbinol from the *n*-undecyl magnesium bromide–ethyl carbonate reaction is of considerable interest. After several recrystallizations from ice-cold ether it had m.p. 75·5° to 76° C. Found: C, 81·3; H, 14·0. Calculated for $C_{23}H_{48}O$: C, 81·1; H, 14·2 per cent. It was apparently produced by reduction of di-*n*-undecyl ketone by " hydrogen magnesium bromide " produced in reaction (vii).

The scheme of reactions may be represented as [26]:



. . . (viii)

By analogy and from the results of Ivanoff's work,[3] the reaction with carbon dioxide may be scheduled as follows:



. . (ix)

Use of Acetylenic Grignard Compounds

Sodiohept-1-ine $C_5H_{11}C{\equiv}CNa$ could not be caused to react with di-*n*-heptyl ketone in liquid ammonia, but *n*-amylacetylene magnesium bromide gave a fairly good yield of di-*n*-heptyl-*n*-heptinyl carbinol with the ketone. The acetylenic Grignard compound $C_5H_{11}C{\equiv}C.MgBr$ was prepared by adding 19 g of *n*-hept-1-ine (made by the action of sodio acetylene on *n*-amyl bromide in liquid ammonia) [27] to its equivalent of ethyl magnesium bromide in di-*n*-butyl ether solution. To this solution was added 55 g of di-*n*-heptyl ketone (made by catalytic decarboxylation of *n*-caprylic acid in presence of thoria at 350° C) and the solution heated to 90° C for 36 hr. Isolation of the carbinol gave 30 g of a very viscous unsaturated oil $(C_7H_{15})_2C(OH).C{\equiv}C.C_5H_{11}$, b.p. 204° to 208° C at 12·5 mm, and in addition 10 g of the ketone, b.p. 180° C at 12·5 mm, were recovered.

The oil was dehydrated catalytically with iodine, and on careful fractional distillation 21 g of the faintly yellow acetylene, b.p. 159° to 160° C at 0·6 mm, were obtained. This enine

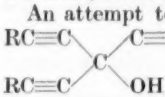
$$(C_7H_{15})(C_6H_{13}CH{:})C.C{\equiv}C.C_5H_{11}$$

would not undergo the Diels–Alder [28] condensation with maleic anhydride.

Dr Braude of the Imperial College of Science and Technology kindly measured the ultra-violet absorption spectra of the carbinol and its dehydration product. The spectra were of the expected types, although the maximum intensity in the case of the enine was very low, probably due to the bulky alkyl substituents. In addition, it could be shown that 5 to 10 per cent dehydration of the carbinol had taken place during distillation.

Hydrogenation of the vinylacetylene with Adams catalyst under pressure gave tri-*n*-heptylmethane, identical with that obtained by the ethyl carbonate method as evidenced by its b.p. 154° to 155° C at 0·4 mm (see Table II).

An attempt to synthesize a carbinol of the type



by the action of sodioheptine or heptine magnesium bromide on ethyl carbonate failed. Brittle red solids were obtained from the reaction mixtures.

The Action of Alkyl Magnesium Bromides on Palmitone [29] $(C_{15}H_{31})_2CO$

Although *n*-butyl magnesium bromide gave di-*n*-pentadecyl-*n*-butylcarbinol in fairly good yield, the

higher homologues gave a most unsatisfactory series of reaction products with palmitone. In all probability these were mixtures containing unchanged ketone, di-*n*-pentadecylcarbinol (obtained by reduction—see p. 40), the desired tertiary alcohol, and the primary alcohol obtained by oxidation of the Grignard reagent as in reaction (vi).

Di-*n*-pentadecyl-*n*-butylcarbinol was obtained as a white solid, m.p. 42·5° to 43° C, after crystallizing several times from alcohol.[29a]

Found : C, 82·4; H, 14·1. Calculated for $C_{35}H_{72}O$: C, 82·4; H, 14·2%.

The series of reactions was not pursued further.

Derivatives of the Carbinols

Attempts to prepare 3 : 5-dinitrobenzoates [30] and the acid tetrachlorophthalates [31] failed. Mixing equimolecular proportions of carbinol and phenyl-*iso*cyanate in a test tube, adding a few drops of triethylamine in dry ether, and placing in a desiccator * in a thermostat at 40° to 50° C for several weeks gave a product which was warmed on a steam bath for 30 min, cooled, boiled with 40° to 60° C ligroin, filtered to remove diphenylurea and allowed to crystallize, or evaporated and the waxy solid recrystallized from ice-cold ethyl alcohol, until constant in melting point. The melting points were sharp, and the phenylurethanes [32] gave good figures on analysis for nitrogen.

Table I summarizes details of the preparation of the carbinols by the various methods.

Preparation of the Olefins

The carbinols were either dehydrated by heating to 150° C with a 50 per cent excess of anhydrous oxalic acid [3] followed by washing with alkali and drying over calcium chloride, or, more conveniently, by placing a few crystals of iodine [4] in the carbinol in the boiler of the fractional distillation apparatus. By the time the column had come to equilibrium (an hour in most cases) dehydration was complete. All the iodine distilled with the lower fractions, and the olefin distilled as a water-white viscous oil. The distillation was repeated, and the overall yield after two distillations was reduced to 70 to 80 per cent of pure olefin, calculated on the weight of carbinol used.

Derivatives of the olefins were, in general, impossible to prepare, or were oils. Thus, the dibromides were all viscous oils, soon darkening on standing. The nitrosyl chloride compound [33] of 4-*n*-propyl-*n*-hept-4 : 5-ene was prepared by treatment of the olefin with ethyl nitrite, 36 per cent hydrochloric acid and glacial acetic acid. After standing seven days in the refrigerator crystals which had slowly formed in the green solution were separated, and after several crystallizations from ethyl acetate had a constant melting point of 86·5° to 87·5° C.

Since this material decomposed on long standing, it was treated with piperidine in a little alcohol. A product of constant m.p. 111° to 112° C was obtained after a few precipitations with 50 per cent aqueous ammonia from acetic acid solution, and possibly consisted of the nitrolpiperidide.

No other olefin gave a nitrosyl chloride derivative, even on very long standing.

Preparation of the Tertiary Methanes

The hydrogenation of the olefins dissolved in glacial acetic acid was carried out using a catalyst composed of 0·5 g palladium deposited by reduction on 15 g of previously dried animal charcoal.[5] The rate of absorption for each reduction was found to obey the zero order law, except in a few cases where "poisoning" was suspected, when Adams platinum oxide catalyst under 60 atmospheres pressure of hydrogen was used.[6] In all cases, slightly more hydrogen was absorbed than was predicted from theory.

The hydrocarbons were isolated by distillation of the solvent, and the residual colourless oil fractionally distilled. Remarkably sharp boiling points were found in all cases, although all the higher members possessed a faint yellow colour. Some of these were analysed and gave excellent figures.

Purification of the Tertiary Methanes

Since the tertiary methanes were required for physico-chemical measurements, stringent purification was necessary.

The two methods attempted were the use of the "molecular still" [10] and adsorption on a silica-gel column.[11] A very simple "pot still" was able to produce steadily at ten drops per min completely colourless specimens of tri-*n*-heptyl and tri-*n*-nonylmethanes, under a vacuum of less than 10^{-6} cm. In each case three fractions were obtained : (1) the lowest, representing 10 per cent of the whole, which was a distinct yellow colour and showed unsaturation towards tetranitromethane ; [34] and (2) two equal portions representing the remainder of the oil. These showed practically identical physical constants and no unsaturated properties. No resin remained in the still.

Tri-*n*-dodecylmethane $(C_{12}H_{25})_3CH$ was too involatile to be distilled through the high efficiency column, and was suspected of containing a small quantity of the solid di-*n*-dodecyl ketone $(C_{12}H_{25})_2CO$. This specimen was unsuitable for molecular distillation, and a very simple adsorption experiment was carried out. The viscous yellow oil was drawn by suction through a vertical ¾-inch bore tube packed with <100-mesh activated silica gel. The oil-soaked column, approximately 9 inches long, was cut into three portions, two of 10 per cent each and a central one of 80 per cent. Each was extracted separately with petroleum ether, which was finally evaporated. The oil from the upper portion solidified

* A convenient desiccator was made from a radio valve cover fitted with a rubber bung. A filter disk to fit the cover rested on a cushion of glass wool thoroughly soaked in concentrated sulphuric acid at the bottom, and on it were placed the reaction tubes.

Table I

Preparation of the Tri-n-alkylcarbinols

Normal alkyl group	Grignard reagent		Carbonyl reagent														Phenylurethanes		
			Carbon dioxide					Corresponding ethyl ester					Ethyl carbonate					M.p., °C	Nitrogen content, %	
	Gram mol of Mg and RBr	Vol of ether, ml	Vol, l	Addition time, hr	Reflux time, hr	Yield, %	B.p. of product	Quantity, gram mol	Addition time, hr	Reflux time, hr	Yield, %	B.p. of product	Quantity, gram mol	Addition time, hr	Reflux time, hr	Yield, %	B.p. of product		Calculated	Found
Propyl	1·0	450	8·0	1·0	14	43	91° to 92° 17 mm	—	—	—	—	—	—	—	—	—	—	75 to 76 [a]	—	—
	1·55	600	—	—	—	—	—	0·75	3·0	18	68	90° to 91° 16 mm	—	—	—	—	—	—	—	—
	3·0	1350	—	—	—	—	—	—	—	—	—	—	1·0	2·0	5·0	73	89·5° to 90° 17 mm	—	—	—
Butyl	1·5	600	12·0	1·5	14	41	126° to 127° 15 mm	—	—	—	—	—	—	—	—	—	—	83·5 to 84·5	4·4	4·7
	6·0	2600	—	—	—	—	—	—	—	—	—	—	2·0	1·5	4·0	54 [b]	114·5° to 115° 10 mm	—	—	—
Amyl	1·5	630	12·0	1·5	14	39	165° to 167° 20 mm	—	—	—	—	—	—	—	—	—	—	73·5 to 74·5	3·7	4·2
	1·33	500	—	—	—	—	—	0·64	2·5	14	57	154° to 155° 11 mm	—	—	—	—	—	—	—	—
Hexyl	1·75	800	—	—	—	—	—	—	—	—	—	—	0·58	1·0	16	55	193° to 194° 20 mm	54 to 55	3·5	3·8
Heptyl	0·67	700	—	—	—	—	—	—	—	—	—	—	0·22	0·5	20	48	165° to 166° 0·4 mm	— [c]	—	—
Octyl	0·5	300	3·5	0·5	14	—	110° to 120° [d] 0·02 mm	—	—	—	—	—	—	—	—	—	—	—	—	—
	0·5	140	—	—	—	—	—	—	—	—	—	—	0·16	0·5	12	35	186° to 188° 0·08 mm	40 to 41 [c]	—	—
	0·5	140	—	—	—	—	—	—	—	—	—	—	0·16 [f]	0·5	12	37	188° to 190° 0·12 mm	—	—	—
	1·0	600	—	—	—	—	—	—	—	—	—	—	0·33	1·0	12	57	186° to 188° 1·0 mm	—	—	—
Nonyl	1·12	700	—	—	—	—	—	—	—	—	—	—	0·37	1·0	10	55	209° to 210° [g] 0·6 mm	—	—	—
Decyl	1·20	800	—	—	—	—	—	—	—	—	—	—	0·40	1·5	18	54	255° to 256° 0·3 mm	50·5 to 51	2·5	2·3
Undecyl	0·8	1000	—	—	—	—	—	—	—	—	—	—	0·27	1·0	12	45	242° to 243° [g] 0·6 mm	—	—	—
Dodecyl	0·38	350	—	—	—	—	—	—	—	—	—	—	0·12	0·5	15	40	245° to 246° [g] 0·4 mm	—	—	—
	0·38	200 [h]	—	—	—	—	—	—	—	—	—	—	0·12	0·5	15	19	250° to 251° 0·6 mm	—	—	—

Notes: [a] This phenylurethane has already been described [9].
[b] Approximately 30% of this carbinol was lost, due to dehydration.
[c] No phenylurethane could be isolated.
[d] This was the highest fraction obtained in this experiment.
[e] Insufficient material to obtain constant m.p.
[f] Chloroformic ester used instead of ethyl carbonate.
[g] No carbinol isolated, due to complete dehydration; yield based on production of olefin.
[h] Experiment carried out in di-*n*-butyl ether at 140° C.

on standing, and was presumably the ketone, while that from the central colourless portion possessed physical constants identical with those expected for tri-*n*-dodecylmethane, within the limits of experimental error. The third section was not investigated further.

It should be noted that no solvent or temperature control were used before cutting the column, and the oil was completely adsorbed on the silica gel.

Physical Constants of the Tertiary Methanes

Melting points were not determined, as they were always below 0° C.

(a) *Density.* Densities at 20° C with respect to water at 4° C were measured, using an approximately 10-ml pyknometer. Comparison of densities of impure and purified hydrocarbons showed very little difference between such specimens, making this property a poor one as a criterion of purity. In general, the densities of tri-*n*-alkylmethanes are greater than those of their normal analogues, and a graph of density against carbon content gave a convex curve, apparently tending to a maximum.

(b) *Surface tension and parachor.* These constants were measured in the "maximum bubble pressure" apparatus,[12] using pure benzene of known surface tension as a standard. Parachors were calculated from the formula

$$[P] = \frac{M\gamma^{\frac{1}{4}}}{d_4^{20}}$$

and compared with those evaluated from Sugden's atomic parachors (C = 4·8, H = 17·1). Correspondence was good, and identity of the products was established.

(c) *Refractive index* n_D^{20} *and molecular refraction* $[R_L]_D$. The former constants were measured at 20° C in an Abbé refractometer, using the sodium D line. The molecular refractions were calculated from the Lorenz–Lorentz equation

$$[R_L]_D = \frac{n^2 - 1}{n^2 + 2}\frac{M}{d}$$

Differences between impure and purified specimens were very small in all cases for both constants.

TABLE II

Properties of the Hydrocarbons

Parent carbinols	Alkenes			Alkanes											
	Dehydrating agent	Yield, %	B.p.	B.p.	Catalyst	Analysis		$d_4^{20} \times 10^3$	Surface tension γ, (dynes/cm)	Parachor $[P] = \frac{M\gamma^{\frac{1}{4}}}{d_4^{20}}$		n_D^{20}	ε	$[R_L]_D$	P
						Calculated, %	Found, %			Calculated[b]	Found				
Tri-*n*-propyl	Oxalic acid	71	54° 15 mm	157° 750 mm	Pd/C	—	—	7359	23·14	424	423	1·4140	1·9955	48·31	48·17
Tri-*n*-butyl	Oxalic acid	73	92° to 93° 14 mm	88·8° to 90° 10 mm	Pd/C	—	—	7610	25·22	542	542	1·4272	2·0319	62·22	62·00
Tri-*n*-amyl	Oxalic acid	70	137° to 138° 14 mm	126° to 126·5° 9 mm	Pd/C	—	—	7762	25·94	658	658	1·4350	2·0540	76·12	75·84
Tri-*n*-hexyl	Iodine	77	169° to 170° 17 mm	162° to 162·2° 10 mm	Pd/C	—	—	7877	27·13	775	775	1·4410	2·0715	90·02	89·71
Tri-*n*-heptyl	Iodine	75	159° to 160° 0·5 mm	156° to 158° 0·6 mm	PtO_2	—	—	7962	—	—	—	1·4464	2·1014	104·11	104·76
Tri-*n*-octyl	Oxalic acid Iodine	68 70	184·6° 0·4 mm 184° to 185° 0·4 mm	182·4° 1·0 mm	Pd/C	C, 85·1 H, 14·9	C, 85·7 H, 14·4	8028	28·77	1010	1010	1·4488	2·1061	117·78	118·33
Tri-*n*-nonyl	Iodine	55[a]	209° to 210° 0·6 mm	196·5° to 197·5° 0·35 mm	Pd/C	C, 85·2 H, 14·8	C, 85·3 H, 14·7	8095	—	—	—	1·4525	2·1020	131·67	131·08
Tri-*n*-decyl	Iodine	80	225° to 227° 0·9 mm	225° to 227° 0·9 mm	PtO_2	C, 85·2 H, 14·8	C, 85·3 H, 14·4	8124	—	—	—	1·4538	2·1255	145·55	146·69
Tri-*n*-undecyl	Iodine	48[a]	242° to 243° 0·6 mm	239° to 241° 0·4 mm	PtO_2	C, 85·2 H, 14·7	C, 85·5 H, 14·5	8153	—	—	—	1·4556	2·1114	159·55	158·78
Tri-*n*-dodecyl	Iodine	40[a]	250° to 251° 0·4 mm	245·5° to 246·5° 0·4 mm	PtO_2	—	—	8193	—	—	—	1·4576	2·1203	173·38	172·89

[a] Yield based on quantity of RMgBr made initially, since dehydration took place during distillation.
[b] Calculated from C = 4·8, H = 17·1. [c] Experimental value.

Refractive indices were slightly greater than those of the corresponding normal isomers up to C_{19}, but falling regularly to reach, for the higher members, a constant difference of 0·0008 less than the extrapolated values for the straight-chain paraffins of high molecular weight (using the series constants given by Audsley and Goss).[35] Densities for the trialkylmethanes are, however, greater in all cases, and consequently the molecular refractions showed a small negative exaltation when compared with the normal isomers. This is to be expected, due to the presence of the tertiary carbon grouping.

Refractive indices displayed a convex curve tending to a maximum when plotted against carbon content.

(d) *Dielectric constant,* ε, *and polarization,* P. A silvered condenser cell, calibrated against pure benzene

and chloroform, was filled with the specimen under investigation, and its electrical capacity was measured by placing it in parallel with the standard condenser of a heterodyne circuit. The dielectric constant could then be calculated by simple proportionality. Accuracy was as great as 1 in 10^4 in a 40-ml cell and 3 in 10^4 in a 11-ml cell.

Measurements of the dielectric constant for the impure specimens gave very high values. Subsequent purification and remeasurement gave values which differed from those for the normal isomers in the same way as was found for the refractive indices (see above) while values found for the low-boiling fractions were increased considerably. Purification by the methods indicated on pp. 37 and 41 was continued until the dielectric constants could be reduced no further.

A smooth convex curve was obtained when the dielectric constant was plotted against carbon content for specimens of guaranteed high purity. The curve compared well with that derived from theoretical considerations.

Polarizations were calculated from the formula

$$P = \frac{\epsilon - 1}{\epsilon + 2} \frac{M}{D}$$

and for the very pure hydrocarbons were slightly less than those of the normal isomers, this negative exaltation being equal to that of the molecular refraction.

Electrical properties were measured immediately after purification, and samples bottled as soon as possible to avoid formation of peroxides, which would influence all the properties. The presence of these air-oxidation products was detected in the case of several pure samples that had been standing some time, by the pink colour produced in the ferrous sulphate–potassium thiocyanate test.

The optical and electrical properties are tabulated, and their significance discussed, in the succeeding communication.

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RELATIONSHIPS BETWEEN THE MOLECULAR VOLUME, REFRACTION, AND POLARIZATION OF THE TRI-*N*-ALKYLMETHANES *

By A. AUDSLEY, † F. R. GOSS, ‡ and DONALD A. PANTONY ¶

SYNOPSIS

The molecular refractions of the series of symmetrical tri-*n*-alkylmethanes from 5-*n*-butylnonane to 13-*n*-dodecylpentacosane have been obtained and show a constant increment for each addition of $(CH_2)_2$. This is slightly lower than the corresponding increment for the straight-chain paraffins. The exaltations for the complete series of trialkylmethanes from *iso*butane do not, however, have a constant value, but when plotted against the number of carbon atoms exhibit a discontinuity at 3-ethylpentane. This discontinuity is also exhibited by other physical properties such as the density. For these reasons, the properties of 4-*n*-propylheptane are slightly anomalous when compared with the higher members of the series. The phenomena associated with the discontinuity are due, partly to the measurement of the physical properties at 20° instead of at "corresponding temperatures," and partly to the fact that whereas the boiling points of the series of *n*-paraffins lie on a smooth curve, those of any homologous branched-chain series exhibit a discontinuity when the longest carbon chain approaches five atoms.

Polarizations derived from the dielectric constants of the trialkylmethanes have the same exaltations as the refractions, and are employed throughout the investigations as a sensitive indication of the purity of the hydrocarbons investigated.

AUDSLEY and Goss [1] have discussed a difference between the boiling point curves of the straight- and branched-chain paraffins. Those paraffins having two terminal methyl groups (*i.e.*, the normal series from ethane upwards) have boiling points which lie on a single smooth curve. The branched-chain series have boiling points which lie on two distinct smooth curves linked by a discontinuity point which occurs when the longest chain approaches five carbon atoms. This phenomenon, for which corroborative evidence is available from other sources, is attributed to the restriction in the space available for the curling of the chain, when its length reaches five atoms.

This property of the boiling points is most clearly illustrated by the exaltation of the boiling point Δ b.p., a negative quantity which is the difference between the boiling points of isomeric straight- and branched-chain compounds. Such exaltations for the trialkylmethanes are plotted in Fig 1.

Molecular volumes at a fixed temperature such as 20°, the temperature at which our measurements are made, must of necessity exhibit the same phenomenon. As has been explained by Audsley and Goss,[1] the exaltation $\Delta(M/d)$ of the molecular volumes is a function of the corresponding boiling point exaltation, and it will be seen from Fig 1 that the $\Delta(M/d)$ curve is of similar shape to that for Δ b.p. with a discontinuity point at exactly the same position, although the curves are of necessity inverted in direction. This close relationship between molecular volume and boiling point exists partly because both properties are affected, in differing degrees, by the space needed for chain curling, and partly because the decrease of molecular volume between the boiling point itself and the temperature of measurement for any individual member of the series is proportional to the interval between these temperatures. This temperature interval itself is naturally also subject to a discontinuity point.

In the case of the volume refraction or refraction per unit volume $[r = (n^2 - 1)/(n^2 + 2)]$ Audsley and Goss [1] have shown that the value of r is, in part, dependent on an anisotropic parameter which arises from the effect of the asymmetric shape of the molecule on the Lorentz field. The molecular shape is naturally affected by the chain-curling effect, so that the values of r for the individual hydrocarbons are considerably affected near the C_7 member of the series. In addition, the increase of volume refraction over the interval between the boiling point and the temperature of measurement will be dependent on the length of this temperature interval, with its discontinuity point at the same position in the homologous series as in examples already considered. It follows that the curve of volume refraction exaltation (Fig 1) is of the same general shape as those for the other physical properties.

The molecular refraction is the product of molecular volume and volume refraction, $[R] = r \,.\, M/d$, so that for this constant there is again a discontinuity at the same position at C_7 in the homologous series. The molecular refraction is of considerable theoretical interest, but in assessing errors of measurement, especially for the higher members of the series, it is more satisfactory to employ the volume refraction, as this function of the refractive index is free from the wide difference in molecular weight encountered in molecular dimensions.

The molecular and volume polarizations (P_{E+A} and p) derived from the dielectric constants (ε) by the Clausius–Mosotti expression $P_{E+A} = p \,.\, M/d$ [where $p = (\varepsilon - 1)/(\varepsilon + 2)$] have been shown by Audsley and Goss [1] to give exaltations which are equal to the corresponding refraction exaltations. Consequently,

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it is possible from the known polarizations of the straight-chain series and the refraction exaltation measured for the trialkylmethane to predict the value of the polarization for each hydrocarbon. The special importance of the polarization data in the case of the trialkylmethanes lies in the sensitivity of the dielectric

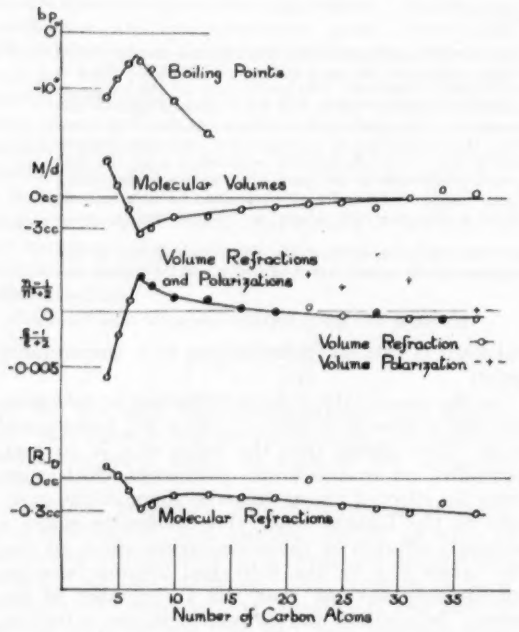

FIG 1

EXALTATIONS AT 20° C FOR THE TRI-*n*-ALKYLMETHANES

constant to small amounts of polar impurities, and the polarizations have been employed in this work mainly as a criterion of the purity of the hydrocarbons investigated.

EXALTATION CURVES FOR THE TRIALKYLMETHANES

In the present work the above conclusions are applied to the symmetrical members of the trialkylmethanes prepared by Challenger and Pantony.[2] These compounds form an extension of the series *iso*butane, 2-methylbutane, 3-methylpentane, 3-ethylpentane, and 3-ethylhexane, in which the alkyl groups of the symmetrical trialkylmethanes are each in turn replaced by the next higher member. To the lower members of this series, Audsley and Goss [1] have applied their boiling point exaltation relationship, finding a discontinuity of physical properties at the C_7 member.

In the extension of this series as far as C_{37}, it is necessary to make use of extrapolated values of M/d and $[R]$ for the normal paraffins, as at 20° these do not remain liquid beyond C_{16}. This can fortunately be achieved with reasonable certainty if it is assumed with Deanesley and Carleton [3] that the increments of molecular volume follow a smooth curve and approach a constant value for the highest members. Wibaut and Langedijk [4] found a constant increment of molecular refraction for the whole range of liquid straight-chain paraffins. For the straight-chain members above C_{16} the following series constants of Audsley and Goss [5] have been taken:

For higher *n*-paraffins:

$$\text{Increment of } M/d_4^{20} = 16{\cdot}327 \quad . \quad . \quad (1)$$

For *n*-paraffins containing *c* carbon atoms

$$[R]_D^{20} = 2{\cdot}09 + 4{\cdot}638c \quad . \quad . \quad . \quad (2)$$

Extrapolated values for the volume refraction of the higher *n*-paraffins are obtained as a quotient from expressions (1) and (2) (see Table I).

The exaltations of molecular volumes and the volume refractions for the higher trialkylmethanes now being considered (Table II) lie close to smooth curves, as do the boiling point exaltations, in so far as they have been measured, at atmospheric pressure (Fig 1). The experimental points for the molecular volumes of the higher members of the series appear to deviate from the mean curve to an increasing extent, but this is due to the large error of calculation arising from the magnitude of the molecular weights.

The polarization of these trialkylmethanes in an electrical field has been treated in the same way as their behaviour in the optical field by making use of the dielectric constants recorded with other experimental data in Table II. Exaltations are obtained by comparing the values for P_{E+A} and the volume polarization with the series values for the *n*-paraffins obtained by Audsley and Goss.[1] These can be expressed for *n*-paraffins containing *c* carbon atoms as indicated in the expression

$$P_{E+A}^{20} = 2{\cdot}24 + 4{\cdot}610c \quad . \quad . \quad . \quad (3)$$

p is obtained as a quotient from expressions (1) and (3).

Audsley and Goss [1] have found that when free from polar impurities the optical and electrical exaltations for each individual branched-chain paraffin should be identical. The coincidence, within the limits of errors of measurement and calculation, of the exaltations of the volume refractions and polarizations (see Fig 1) for all except three of the trialkylmethanes available, indicates a high state of freedom from polar impurities (not more than 0·02 per cent) for the remaining hydrocarbons. Fractional or molecular distillation or separation by chromatographic absorption were used by Challenger and Pantony [2] to remove impurities from the samples of trialkylmethanes measured in this investigation. Measurement of the physical properties, and especially the dielectric constant, indicated at each stage the increasing purity, but the purification could not be continued as far as could have been wished in the

case of the C_{22}, C_{25}, and C_{31} members owing to insufficiency of material.

The exaltations of molecular refraction plotted in Fig 1 can, for the same reasons as apply to the molecular volume, be most accurately calculated for the lower members. The exaltations from C_{13} onwards, which increases in proportion to the molecular weight. This particular source of error is eliminated by considering the volume refraction and polarization, so that comparison of the values of these quantities for a given individual affords the most sensitive test of its purity (Fig 1).

Deviations of both optical and electrical exaltations from the values expected on this basis can be attributed, in the case of C_{22}, C_{25}, and C_{31}, to the presence of not more than 0·5 per cent of polar impurities, but in the constants of the higher members generally there is a small unavoidable error of calculation after due allowance for errors due to impurities, and those inherent in the methods of measurement and calculation, appear to have a constant decrement which has a value of 0·0065*c*. The C_{10} member is exceptional in being influenced by its proximity to the discontinuity point at C_7.

TABLE I

Smoothed and Extrapolated Constants for Certain n-*Paraffins, in the Liquid State at 20° C*

(Expanded from Audsley and Goss [5])

		b.p.	d	n_D	ε	M/d	$\left(\frac{n^2-1}{n^2+2}\right)r_D$	$\left(\frac{\varepsilon-1}{\varepsilon+2}\right)p$	$[R]_D$	P_{E+A}
C_4	*n*-Butane	−0·5	—	—	—	—	—	—	—	—
C_5	*n*-Pentane	36·1	0·6263	1·3578	1·8439	115·19	0·21948	0·21955	25·28	25·29
C_6	Hexane	68·7	0·6594	1·3750	1·8900	130·68	0·22893	0·22880	29·92	29·90
C_7	Heptane	98·4	0·6837	1·3877	1·9241	146·54	0·23582	0·23549	34·56	34·51
C_8	Octane	125·6	0·7026	1·3975	1·9506	162·56	0·24111	0·24064	39·19	39·12
C_9	Nonane	150·7	0·7177	1·4054	1·9722	178·69	0·24531	0·24473	43·83	43·73
C_{10}	Decane	174·0	0·7300	1·4118	1·9896	194·88	0·24872	0·24804	48·47	48·34
C_{13}	Tridecane	235·5	0·7565	1·4256	2·0275	243·68	0·25601	0·25513	62·38	62·17
C_{16}	Hexadecane	286·5	0·7739	1·4347	2·0526	292·60	0·26077	0·25974	76·30	76·00
C_{19}	Nonadecane	—	0·7861	1·4411	2·0706	341·56	0·26413	0·26300	90·21	89·83
C_{22}	Docosane	—	0·7953	1·4460	2·0840	390·53	0·26664	0·26543	104·13	103·66
C_{25}	Pentacosane	—	0·8024	1·4497	2·0946	439·51	0·26858	0·26733	118·04	117·49
C_{28}	Octacosane	—	0·8081	1·4527	2·1033	488·49	0·27014	0·26889	131·96	131·32
C_{31}	Hentriacontane	—	0·8127	1·4552	2·1099	537·47	0·27140	0·27006	145·87	145·15
C_{34}	Tetratriacontane	—	0·8166	1·4572	2·1157	586·46	0·27245	0·27108	159·78	158·98
C_{37}	Heptatriacontane	—	0·8199	1·4590	2·1206	635·44	0·27335	0·27195	173·70	172·81

TABLE II

Physical Properties of the Homologous Series of Trialkylmethanes and their Exaltations Compared with those of the Isomeric n-*Paraffins at 20° C*

		b.p.	d	n_D	ε	Δ b.p.	$\Delta(M/d)$	Δr_D	Δp	$\Delta[R]_D$	ΔP_{E+A}
C_4	*iso*Butane	−12·2	—	—	—	−11·7	(3·5)	—	—	(0·1)	—
C_5	2-Methylbutane	27·9	0·6197	1·3539	—	− 8·2	+1·23	−0·00214	—	0·02	—
C_6	3-Methylpentane	63·2	0·6643	1·3766	—	− 5·5	−0·96	+0·00086	—	−0·11	—
C_7	3-Ethylpentane	93·4	0·6984	1·3935	1·9379	− 5·0	−3·07	+0·00311	0·00268	−0·28	−0·34
C_8	3-Ethylhexane	118·9	0·7136	1·4016	1·9617	− 6·7	−2·49	+0·00217	0·00211	−0·25	−0·26
C_{10}	4-*n*-Propylheptane	161·7	0·7359	1·4140	1·9955	−12·3	−1·56	+0·00116	0·00112	−0·16	−0·17
C_{13}	5-*n*-Butylnonane	218	0·7610	1·4272	2·0319	−18	−1·43	+0·00085	0·00080	−0·16	−0·17
C_{16}	6-*n*-Amyl-undecane	—	0·7752	1·4350	2·0540	—	−0·88	+0·00017	0·00025	−0·18	−0·16
C_{19}	7-*n*-Hexyl-tridecane	—	0·7876	1·4410	2·0715	—	−0·68	−0·00006	0·00017	−0·19	−0·12
C_{22}	8-*n*-Heptyl-pentadecane	—	0·7962	1·4464	*2·1014*	—	−0·42	+0·00023	*0·00311*	−0·02	*+1·10*
C_{25}	9-*n*-Octyl-heptadecane	—	0·8028	1·4488	*2·1061*	—	- 0·24	−0·00046	*0·00205*	−0·26	+0·84
C_{28}	10-*n*-Nonyl-nonadecane	—	0·8095	1·4525	2·1020	—	−0·88	−0·00011	−0·00015	−0·29	−0·24
C_{31}	11-*n*-Decyl-heneicosane	—	0·8124	1·4538	*2·1255*	—	+0·22	−0·00070	*0·00276*	−0·32	*+1·54*
C_{34}	12-*n*-Undecyl-tricosane	—	0·8153	1·4556	2·1114	—	+0·91	−0·00082	−0·00076	−0·23	−0·20
C_{37}	13-*n*-Dodecyl-pentacosane	—	0·8193	1·4576	2·1203	—	+0·44	−0·00069	−0·00005	−0·32	+0·08

Values of physical properties for C_4 to C_8 and of C_{10} are from the literature.
Values for C_{10} to C_{37} are new measurements. The constants italicized are considered to be high, and this is taken to indicate the presence, for C_{22}, C_{25}, and C_{31}, of not more than 0·5% of polar impurity.

The three values for the exaltations $\Delta(M/d)$, Δr, and $\Delta[R]$ for any given trialkylmethane can be related (where $[R]$, r, and M/d represent the values for the corresponding n-paraffins) by the expression

$$[R] + \Delta[R] = [r + \Delta r][(M/d) + \Delta(M/d)]$$

whence

$$\Delta[R] = \Delta r \,.\, M/d + \Delta(M/d) \,.\, r + \Delta r \,.\, \Delta(M/d) \quad (4)$$

The final term in expression (4) is the product of two small quantities, and can be neglected, so that

$$\Delta[R] = \Delta r \,.\, M/d + \Delta(M/d) \,.\, r \quad . \quad (5)$$

By means of expression (5) the various exaltation curves can be correlated with one another. For the highest members of the trialkylmethane series the exaltation of molecular volume becomes so small that it is comparable with the error of measurement, so that for members above C_{30}

$$\Delta[R] = \Delta r \,.\, M/d \quad . \quad . \quad . \quad (6)$$

It will be seen from Fig 1 that after a maximum value at C_7 the curve for Δr falls to a constant value of $-0{\cdot}0004$ for the high members of the series. For these high members the molecular volumes are nearly identical with those of the extrapolated values for the straight-chain series, so that by combining expressions (1) and (6), $\Delta[R]$ should, at least for the trialkylmethanes above C_{30}, be a constant fraction of the molecular volume, and should have a constant negative increment of $0{\cdot}0065c$. This decrement has actually been established for the whole series from C_{13} onwards.

The linear portion of the $\Delta[R]$ curve has the value $-0{\cdot}08 - 0{\cdot}0065c$, and the decrement of 0·0065 must be due primarily to the anisotropic parameter x' employed by Audsley and Goss [1, 5] to express differences in physical properties of the gaseous and liquid states. Their conclusion is that, as in the gaseous state the increment of molecular volume should be a constant, the exaltation of molecular refraction should also be constant. In the liquid state, however, the anisotropy, and change in molecular volume increment, should result in a progressive change in the increment of molecular refraction, as is now confirmed by the decrement found for the trialkylmethane series.

CALCULATION OF SMOOTHED PHYSICAL PROPERTIES FROM THE EXALTATION CURVES

From the mean curve (Fig 1) for the exaltations of molecular volume of the trialkylmethanes combined with the smoothed values for the increments of molecular volume for the n-paraffins (Table I), it is a simple matter to obtain the density expected for any compound in the branched-chain series. Similarly, the smoothed refractive index and dielectric constant may be obtained by combining the expressions (2) and (3) for the molecular refraction and polarization of the n-paraffins with the smoothed exaltation $-0{\cdot}08 - 0{\cdot}0065c$ for the higher members of the present series obtained from their mean curves.

For example, as P_{E+A} for the n-paraffins is $2{\cdot}24 + 4{\cdot}61c$ and ΔP_{E+A} for the higher trialkylmethanes is $-0{\cdot}08 - 0{\cdot}0065c$, P_{E+A} for the higher trialkylmethanes should be $2{\cdot}16 + 4{\cdot}6045c$. Now, $P_{E+A} = (\varepsilon - 1)M/(\varepsilon + 2)d$, so that $\varepsilon = [(M/d) + 2P_{E+A}]/[M/d - P_{E+A}]$, which in this case is $[(M/d) + 4{\cdot}32 + 9{\cdot}209c]/[(M/d) - 2{\cdot}16 - 4{\cdot}6045c]$. Similarly n is $[(M/d) + 4{\cdot}02 + 9{\cdot}263c]^{\frac{1}{2}}/[(M/d) - 2{\cdot}01 - 4{\cdot}6315]^{\frac{1}{2}}$. The smoothed constants given by these expressions (Table III) with the experimental values given in Table II are plotted in Fig 2. These curves clearly show the discontinuity at C_7 and also that the dielectric constant is so sensitive to the presence of polar impurities that it is greatly to be preferred for their detection than either density or refractive index. For density and refractive index the observed and smoothed values do not differ by more than 0·001 in any instance, but the dielectric constants permit the separation of the specimens into two classes. For the majority, the observed and smoothed values do not differ by more than 0·002. This is comparable with the experimental error, but, on the other hand, for the three members C_{22}, C_{25}, and C_{31}, where insufficient material was available for complete

TABLE III

Smoothed Constants for the Homologous Series of Trialkylmethanes, at 20° C

		d	n_D	ε	M/d	$\frac{r_D}{\left(\frac{n^2-1}{n^2+2}\right)}$	$\frac{p}{\left(\frac{\varepsilon-1}{\varepsilon+2}\right)}$	$[R]_D$	P_{E+A}
C_{10}	4-*n*-Propylheptane	0·737	1·414	1·997	193·1	0·2502	0·2495	48·31	48·18
C_{13}	5-*n*-Butylnonane	0·760	1·427	2·031	242·5	0·2566	0·2557	62·23	62·01
C_{16}	6-*n*-Amylundecane	0·776	1·435	2·055	291·7	0·2609	0·2603	76·12	75·82
C_{19}	7-*n*-Hexyltridecane	0·788	1·441	2·070	340·9	0·2641	0·2629	90·01	89·63
C_{22}	8-*n*-Heptylpentadecane	0·796	1·446	2·083	390·1	0·2664	0·2652	103·91	103·44
C_{25}	9-*n*-Octylheptadecane	0·803	1·449	2·093	439·2	0·2683	0·2670	117·80	117·25
C_{28}	10-*n*-Nonylnonadecane	0·808	1·452	2·101	488·3	0·2697	0·2684	131·70	131·06
C_{31}	11-*n*-Decylheneicosane	0·813	1·454	2·108	537·3	0·2710	0·2697	145·59	144·87
C_{34}	12-*n*-Undecyltricosane	0·817	1·456	2·114	586·3	0·2721	0·2707	159·49	158·68
C_{37}	13-*n*-Dodecylpentacosane	0·820	1·458	2·118	635·3	0·2730	0·2716	173·38	172·49

purification, the observed dielectric constants of the samples were found to be too high by 0·019, 0·013, and 0·018 respectively. These small but definite differences between observed and predicted dielectric

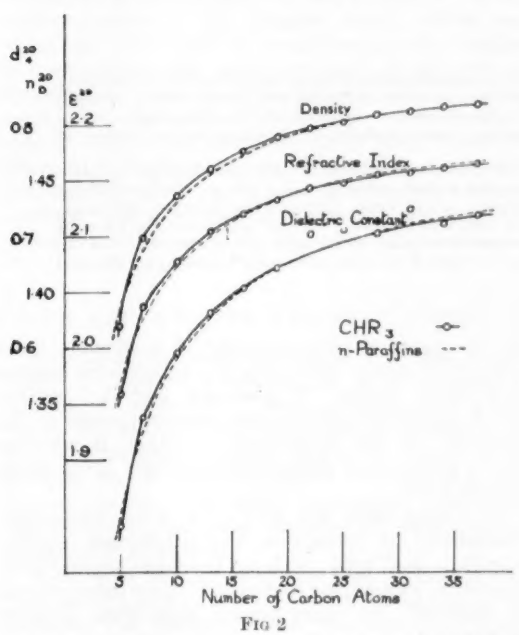

FIG 2

MEAN CURVES OF PROPERTIES FOR THE TRI-*n*-ALKYL-METHANES AT 20° C

constants must indicate that these three samples contain not more than 0·5 per cent of ketones and/or carbinols.

PREVIOUS DETERMINATION OF PHYSICAL CONSTANTS OF THE HIGHER SYMMETRICAL TRIALKYL METHANES

Certain of these hydrocarbons have been prepared previously and their densities and refractive indices recorded. Dielectric constants were not previously known. Where physical constants have been determined at 20° C, the values are in reasonable agreement with those recorded in this paper.

4-Propylheptane was recorded by Eykman (*cf* Ward and Kurtz [6]) d_4^{20} 0·7360, n_D^{20} 1·4141, and by Butler (*cf* Doss [7]), d_4^{20} 0·7364, n_D^{20} 1·4150. 5-Butylnonane was prepared by Ivanoff.[8] 9-Octylheptadecane, d_4^{20} 0·8017, n_D^{20} 1·4487, and 11-decylheneicosane, d_4^{20} 0·8115, n_D^{20} 1·4543, by Cosby and Sutherland.[9] 10-Nonylnonadecane was prepared by Strating and Backer,[10] and by McKittrick *et al.*[11]

PHYSICAL MEASUREMENTS

Refractive indices were measured with an Abbé refractometer using a sodium source. Dielectric constants were determined as described by Goss [12] using a small dielectric cell of air capacity 21 μμ F because the amount of material available was limited. The limit of error of this cell has been lowered by improved technique, so that small dielectric constant values are reproducible to ±0·001. The fourth decimal place is included in the results for comparative purposes, but we do not consider that it has any absolute significance. Densities were measured with an Ostwald–Sprengel pyknometer, and temperatures were kept constant to 20° ± 0·05° C, which corresponds to a change of one unit in the fourth decimal place for the various properties examined.

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ION EXCHANGE RESINS IN HYDROCARBONS*

By ANDREW GEMANT†

SYNOPSIS

The purpose of the study was to establish some basic facts on the action of synthetic ion exchange resins on organic ions in hydrocarbons, including oils. The solutions used were acid–amine–phenol systems, previously found possessing increased electric conductivity. Both cation and anion exchange resins were studied. A radio-active tracer technique, using carbon-14 labelled tridecylic acid, and aniline, was employed for determining the extent of exchange.

The exchange capacity of moist cation exchange resins in hydrocarbons is about 4 milliequivalents per g (same as in water), whereas that of anion exchange resins is only about 0·03 milliequivalent per g. Dehumidifying reduces both figures appreciably. Addition of an acid to a base, or vice versa, increases the extent of exchange, probably because of the increased activity of the salt-like complex formed. Further addition of a phenolic compound reduces the exchange in most cases, probably because of solvation of the acid–amine complex. In the same manner, the extent of exchange decreases in a series of hydrocarbons with increasing solubility of the acid or base in the various members of the series.

PURPOSE OF THE STUDY

THE purpose of the experimental study described in this paper was to obtain some information on the action of ion-exchange resins in hydrocarbons. The major portion of the literature [1] refers to aqueous systems, with a few studies concerning alcohols,[2] inorganic ions in non-aqueous liquids,[3,4] and some patents concerning purification of hydrocarbons.[5] A basic study on the action of synthetic ion-exchangers on organic ions in hydrocarbons, including oils, appeared, therefore, of interest.

An opportunity for such a study has presented itself by the writer's recent studies [6] concerning acid–base systems in hydrocarbons. These studies indicated that such acid–base solutions exhibit relatively high electrical conductivities, and hence contain chemically fairly well defined cations and anions. Such solutions thus offered a suitable object for establishing the extent of ion-exchange on resins in contact with hydrocarbons.

Accordingly, the programme of the study was to find the order of magnitude of the amounts of acid and base adsorbed as a function of certain pertinent variables. Such variables were: the time of adsorption, the nature of the hydrocarbon, the chemical composition and electrical conductivity of the solution, and the moisture condition of the resin.

Having established some experimental facts, an attempt was made to interpret the findings in the light of information obtained from the writer's previous studies concerning these acid–base solutions. These explanations are, of course, by no means definitive, which is the less surprising, as the theory of ion-exchange resins even in aqueous solutions is incomplete to date.

THE RESINS

The ion-exchange resins used in this study were Amberlite resins.‡ Two kinds were used. One was XE-75, being a porous variety of a strongly basic anion exchanger; chemically it is an insoluble organic quaternary amine. It possesses hydroxyl groups which are exchanged for other anions present in the solution. In the as-received condition, it contains about 40 per cent water, which is easily given off in the open air.

The other resin was IR-112, a cation exchanger. Chemically, it belongs to the polystyrene nuclear sulphonic acid type; it is an insoluble organic acid, capable of exchanging hydrogen ions for other cations in solutions. Its water content as-received is about 60 per cent.

As is shown below, both resins were used in moist and dry condition. It was found advisable to have them, when dry, conditioned in an atmosphere of definite low humidity. Saturated lithium chloride solution [7] in contact with the solid maintains a relative humidity of about 15 per cent, and the dry samples were mostly conditioned in such an atmosphere.

THE HYDROCARBON SOLUTIONS

The acid–base solutions in hydrocarbons, referred to above, consisted in the majority of cases of aliphatic acids and organic amines in hydrocarbon solvents or oils. As is explained in the next Section, a radio-active tracer technique was used for measuring the amounts adsorbed; this technique involved a labelled acid and a labelled base respectively.

The labelled acid, used in combination with the anion exchange resin, was tridecylic acid. An aliphatic acid of this kind shows a small increase in electrical conductivity by the addition of a base of medium strength, such as tributylamine or piperidine, and a very large increase upon the further addition of a solvating compound like *o*-cresol.[6] These were the solutes used in the study of anion exchange.

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‡ Amberlite resins are manufactured by Rohm and Haas Company, Philadelphia, Pennsylvania.

The corresponding experiments with cation exchange resin required a labelled organic base of medium strength. The writer did not have the facilities for carrying out the necessary synthesis, and commercially such a base was not available. It was finally decided to use labelled aniline which was available. This had the disadvantage that aniline is a very weak base, and accordingly it does not, in combination with an aliphatic acid and a phenol, yield high electrical conductivities. Even with a strong acid, such as picric acid, only moderate increases in conductivity are obtainable. A range of solutions of widely varying conductivity, such as was used with the anion exchange resin was not available, therefore, in the case of the cation exchange resin.

THE RADIO-ACTIVE TRACER TECHNIQUE

A radio-active tracer technique was used in this study in order to determine the small amounts of compounds adsorbed. Carbon-14 isotope was used for labelling, and the measurements were effected by a thin mica-window Geiger–Müller counter. If the counter for a given geometry is calibrated with known amounts of labelled compounds, counts per minute can be converted directly into micrograms of compounds exchanged.

Samples of resin of 0·1 g were kept in contact with samples of solutions of 1·0 g. After certain times the solution was decanted, and the resin thoroughly washed with benzene, then spread thinly and uniformly on a slide glass which, after a few minutes drying, was placed about 2 mm below the window of the Geiger counter.

For calibration purposes, 0·1-g samples of resin were wetted with a known small amount of benzene containing a known concentration of labelled compound. Table I gives the calibration figures obtained.

TABLE I

Calibration Figures, Giving Counts/Min per μg Compound

Resin	Moisture condition	Labelled compound	Counts/min per μg
XE-75	Moist	Tridecylic acid	7·0
XE-75	Dry	Tridecylic acid	7·0
IR-112	Moist	Aniline	80
IR-112	Dry	Aniline	200

The first figure should be actually smaller than the second, but the difference found was small and uncertain, and was, therefore, disregarded.

As an illustration for a determination, a measured figure of 100 counts/min, after deducting the background, and obtained with a moist XE sample be assumed. Using the calibration figure of 7 of Table I, this is equivalent to 14 μg of labelled tridecylic acid. If the ratio of labelled to total acid concentration in the solution is 20, as was the case in most experiments, altogether 280 μg of acid were exchanged. This corresponds to an adsorbate of 2·8 mg/g of moist resin, or 4·7 mg/g of dry resin. Since the molecular weight of tridecylic acid is 214, the final figure is 22 microequivalents of adsorbate per g of dry resin.

The accuracy of measurements may be estimated to be ±10 per cent. The reproducibility of individual experiments was, however, in a range of, say, ±25 per cent, which is the usual figure obtainable in the field of dielectrics.

RESULTS ON ANION EXCHANGE

In carrying out exchange measurements with XE-75 according to the technique described in the previous Section, it had to be ascertained first that purely mechanical contamination of the highly porous resin with the radio-active solution would not materially increase the readings produced by the adsorbate. In order to check this, control tests were conducted with various tridecylic acid solutions, using XE and IR resins in parallel experiments. Table II gives counts/min observed in such tests. It may be seen that the solution mechanically adhering on IR resin produces in the worst case 10 per cent of the amount adsorbed by XE, but in most cases much less than that.

The effect of time on adsorption is seen from Figs 1 and 2, giving microequivalents of tridecylic acid

TABLE II

Control Tests on Acid Solutions with Both Types of Resin

Counts/min with 0·1-g resin samples. Time: 4 hr

Resin	Solvent	Solutes		
		Acid	Acid + amine	Acid + amine + phenol
XE-75, moist	Transformer oil	87	244	180
IR-112, moist	Transformer oil	0	6	17
XE-75, dry	Xylene	18	—	—
IR-112, dry	Xylene	0	—	—

exchanged per g of dry XE as a function of time. Fig 1 shows an 8-hour run, Fig 2 a 24-hour run, both with moist XE. The rate is high at the beginning, then decreases, and finally approaches zero, as equilibrium is reached. This behaviour is the same as in aqueous systems. A discussion of the three different curves in Fig 2 follows later; here it may be mentioned that the 24-hour figures, which are certainly not too far from the equilibrium values, are of an order of magnitude of 30 microequivalents per g. This figure is appreciably lower than the exchange capacity of 2·8 milliequivalents per g, as given by Kunin *et al* [8] for a similar resin in aqueous solution.

In the majority of the following tests, times shorter than those permitting final equilibrium to be reached were utilized. Whenever, however, longer times were allowed such as in Fig 2, the sequence of exchange

for a given series was the same as for shorter times. A further test, lasting for 160 hr, yielded 27, 39, and 26 microequivalents per g, not too different from the 24-hour figures. Hence, for comparative purposes, the figures in this paper will be considered as representative for the extent of exchange, although it is realized that this procedure would not be satisfactory in considering absolute exchange figures.

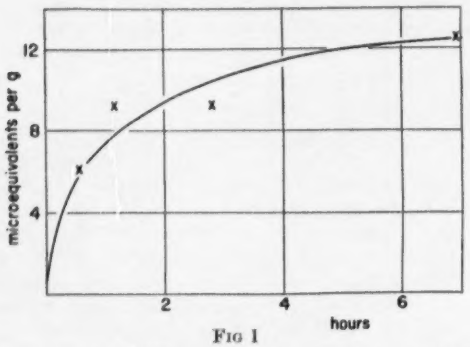

FIG 1

EXCHANGE OF 0·10N TRIDECYLIC ACID IN TRANSFORMER OIL ON MOIST XE-75 RESIN

The effect of solvent and solutes on the extent of exchange is shown in Table III as well as in Fig 2.

TABLE III

Effect of Solvent and Solutes on Acid Exchange

Microequivalents of acid per g resin
Moist XE-75. Time: 2 hr

Solvent	Solutes		
	0·10N tridecylic acid	0·10N tridecylic acid, 0·13N tributylamine	0·10N tridecylic acid, 0·13N tributylamine, 0·20N *o*-cresol
Xylene	9	9	8
n-Octane	11	14	10
Transformer oil	12	20	16
Paraffin oil	16	33	31

The exchange is seen to increase in the order given. A possible explanation is the decreasing solubility of tridecylic acid in the same order. Since solubility and solvation are interrelated, decreasing solvation explains increasing affinity for the resin.

Next, the effect of added solutes may be seen from Table III and Fig 2. Addition of tributylamine to tridecylic acid produces an increase in exchange, further addition of *o*-cresol brings the level down. In the previous studies referred to above [6] it was indicated that the first process in the increase of conductivity is the salt formation between the acid and amine, which in itself does not lead to noticeable ion-formation. The presence of the strongly solvating phenol then leads to noticeable ionic dissociation.

From the present results it can be concluded that ionization of the acid does not lead to increased exchange, since in that case the last column ought to show markedly higher values than the first two. Either the ionic species has no higher affinity for the resin than has the neutral molecule; or the small ratio of ions to the neutral molecules prevents an effect becoming noticeable. The second of these possibilities appears more likely.

The increase of extent of exchange caused by the amine is probably due to the presence of the salt-type compound, the concentration of which is relatively high. One must conclude that the chemical action of the acid–amine compound is stronger than that of the acid alone.

The decrease of exchange by further addition of *o*-cresol is then due to the strongly solvating action of the latter. Just as solvation leads to ionization, it also solvatizes the bulk of the acid–amine compound, thus reducing its affinity to the resin.

The relations in connexion with ion exchange resins are similar to those found by the writer [9] for the formation of salt films on metals immersed in hydrocarbons. There, too, deposits of aliphatic salts on copper, lead, and zinc are promoted by the addition of an amine, while further addition of *o*-cresol in some cases has no effect, in others it definitely decreases the deposit. With both metals and exchange resins in hydrocarbons the effects are explainable on the basis of compound formation and solvation in the hydrocarbons, both processes having been postulated from conductivity studies.

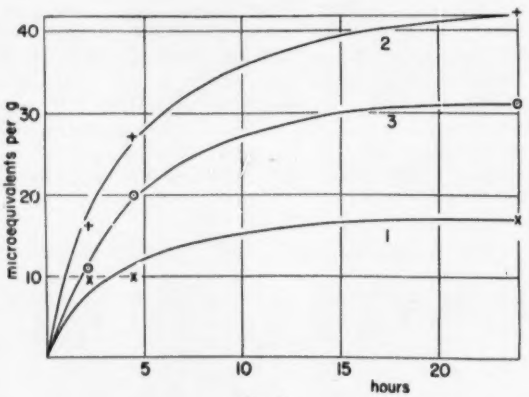

FIG 2

EXCHANGE OF TRIDECYLIC ACID IN TRANSFORMER OIL ON MOIST XE-75 RESIN

1. 0·10N acid
2. 0·10N acid, 0·13N amine
3. 0·10N acid, 0·13N amine, 0·20N *o*-cresol

A few further results concerning the action of the solvating compound are presented in Table IV. In the first and second row comparison between *o*-cresol and benzyl alcohol is presented. Measurements of the electrical conductivity indicate that

both promote ionization, the phenolic compound somewhat more than the alcohol. As for the present effect, both compounds reduce markedly the extent of exchange. The third row in Table IV refers to

TABLE IV

Effect of Solvating Compound on Acid Adsorption

Microequivalents of acid per g resin. Moist XE-75. Transformer oil

Solvating compound	Normality of acid	Time, hr	Solutes			
			Acid	Acid + amine	Acid + solvating compound	Acid + amine + solvating compound
o-Cresol . .	0·10	4	10	27	—	20
Benzyl alcohol	0·10	4	11	25	—	13
o-Cresol . .	0·05	4	8	20	—	13
o-Cresol . .	0·10	5½	—	—	12	—
Benzyl alcohol	0·10	5½	—	—	13	—

an acid concentration half the previous figure; the amounts adsorbed are reduced in a ratio approximately $1 : \sqrt{2}$.

The last two rows refer to mixtures of acid and solvating compound without amine. There is no reduction, rather an increase, compared with the acid alone. It appears that the aliphatic acid alone is not solvated by the phenol or alcohol.

It was of interest to see what effect dehydration of the resin had on the adsorption. As mentioned on page 50, the dehydrated resin was conditioned at 15 per cent relative humidity. As was expected, the extent of adsorption was considerably reduced. Table V shows the results.

TABLE V

Acid Adsorption by Dry XE-75 Resin. Microequivalents of Acid per g Resin

Condition of resin	Solvent	Base	Time, hr	Solutes		
				0·10N acid	0·10N acid + 0·15N base	0·10N acid + 0·15N base + 0·20N *o*-cresol
Dry	Paraffin oil	Tributane amine	4	1·6	0·8	0·6
Dry	Transformer oil	Tributane amine	3	1·9	1·5	0·8
Dry	Transformer oil	Tributane amine	48	5·6	5·1	2·3
Moist	Transformer oil	Piperidine	2½	14	280	170
Dry	Transformer oil	Piperidine	4	2·0	2·3	1·4

As may be seen by comparison with Table III, for instance, the figures for dry resin are appreciably lower than for moist resin. As a matter of fact, the level of 1 microequivalent per g is close to the level at which the significance of the actual figure is in doubt. Addition of a base reduces the figures, that of cresol still more.

The fourth row refers to a test with piperidine, which is a much stronger base than tributylamine, as verified also by conductivity measurements. The exchange figures are correspondingly quite high; drying the resin, however, yields low exchange, even in this case. In order to obtain comparative data on anion exchange, use of the moist resin is obviously preferable to the dehydrated one.

RESULTS ON CATION EXCHANGE

In the series utilizing labelled aniline it had to be ascertained first whether the error introduced by mechanical adherence of the solution was not excessive. Parallel experiments using both IR-112 and XE-75 in a 0·031N aniline solution were carried out; the ratio of labelled to total aniline concentration was 1 : 440. Table VI gives the results. Similarly to acid

TABLE VI

Control Tests on Basic Solution with Both Resins

Counts/min with 0·1 g resin samples, 0·031N-aniline in xylene

Resin	Time, min	Counts/min
IR-112, moist	6	607
XE-75, moist	6	39
IR-112, dry	30	41
XE-75, dry	30	5

adsorption, the control tests yield a much lower count, indicating that the measured counts with IR-112 may be from 6 to 12 per cent higher than the true counts.

Adsorption *vs* time is shown in Fig 3, which refers

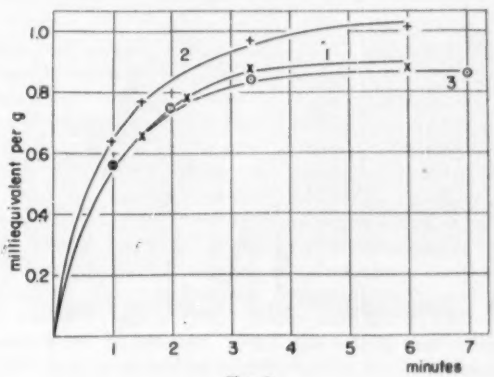

FIG 3

EXCHANGE OF ANILINE IN XYLENE ON MOIST IR-112 RESIN

1. 0·03N aniline
2. 0·03N aniline, 0·20N propionic acid
3. 0·03N aniline, 0·20N propionic acid, 0·20N *o*-cresol

to tests with moist IR-112 and labelled aniline solutions in xylene. Two differences as compared with XE resin and aliphatic acid may be noted. One is that the exchange is much faster. In this particular instance about 6 minutes appeared sufficient to complete the process. The other difference is the larger extent of exchange as compared with XE resin. About the total amount of aniline available in the liquid was taken up in this case. There is only little difference between the three curves, referring to added propionic acid and *o*-cresol; because of the

large amount of exchange, secondary differences of this nature are not evident. Another, similar test, providing more aniline available in the liquid, gave 4·7 milliequivalents per g dry resin as exchange capacity, a figure in close agreement with that found in aqueous systems.[6]

It seemed advisable to carry out further measurements with dehumidified IR-112. Fig 4 shows the

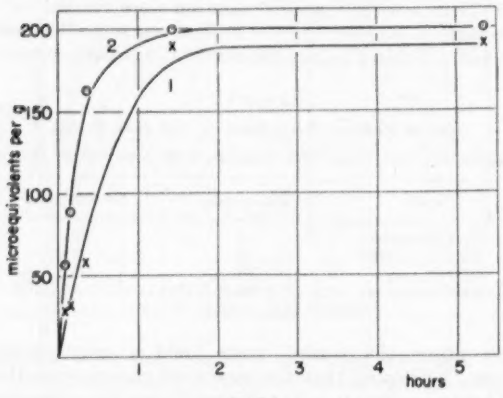

FIG 4

EXCHANGE OF ANILINE IN XYLENE ON DRY IR-112 RESIN

1. 0·03N aniline
2. 0·03N aniline, 0·001N picric acid, 2 per cent ethyl alcohol

time dependence. The rate is fast also in this case, although not as fast as in Fig 3; equilibrium appears to be reached in about 80 minutes. The final value is some 200 microequivalents per g. It is interesting that dry IR, although reduced in activity, is still effective, while the capacity of dry XE, as mentioned on page 51, was found to be very low.

Addition of a small amount (0·001N) of picric acid and 2 per cent ethyl alcohol, by which means the electrical conductivity is increased, produces marked increase of exchange in the earlier stages, not pronounced in the final value. Only a small fraction of aniline was in the salt form; because of the limited solubility of the picrate, larger additions of picric acid are not feasible.

Table VII presents the results obtained with the dehumidified cation exchange resin, employing aliphatic acids to form salts. Propionic acid is one of the strongest oil-soluble members of that group, the di-bromo compound is even stronger in water. The results are altogether comparable to those of Table III, the figures increasing with decreasing solubility in the respective hydrocarbons. Addition of propionic acid—like picric acid (see Fig 4)—promotes

TABLE VII

Effect of Solvent and Solutes on Base Adsorption

Microequivalents of base per g resin. Dry IR-112

Solvent	Concentration of aniline	Acid	Time, min	Solutes		
				Aniline	Aniline, 0·20N acid	Aniline, 0·20N acid, 0·20N *o*-cresol
Dioxane .	0·03N	di-Br-propionic	10	26	29	—
Xylene . .	0·03N	Propionic	10	27	41	49
Xylene . .	0·09N	Propionic	70	61	103	90
Transformer oil	0·03N	Propionic	10	120	160	160

the extent of exchange; the effect of the solvating compound being rather variable. It will be of probable interest to study the exchange properties of IR resins, using a stronger base than aniline, like tributylamine, for instance.

PRACTICAL APPLICATION

While the purpose of this study is, as mentioned above, the finding of certain fundamental facts, in conclusion a few words may be added concerning the applicability of exchange resins in hydrocarbons. The figures obtained show that removal of acidic and basic compounds from hydrocarbons is, indeed, possible by this method. Generally, it would be more advisable to use the dehydrated product, since moist resins might introduce water into the organic phase, which in certain cases, liquid dielectrics, for instance, is undesirable. This condition can be satisfied with the cation exchange resin, which, when dehumidified, still shows satisfactory exchange capacity. With the anion exchange resin, however, the capacity in the dry condition drops to very low values, for which reason use of the moist resin appears preferable.

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THE SUNBURY X-RAY ABSORPTION METHOD FOR THE RAPID DETERMINATION OF SULPHUR IN HYDROCARBONS *

By R. W. CRANSTON, F. W. H. MATTHEWS, and N. EVANS

SUMMARY

This paper presents a method for the determination of sulphur by means of X-ray absorption. The method has been developed to meet the need in the control of refinery processes for a rapid and, at the same time, a reasonably accurate method for the determination of sulphur in petroleum and its products. The average time required for a single determination on a distillate sample is about 5 minutes and for residual samples 5 to 15 minutes, depending on the viscosity and hence the time required to fill the cell. The accuracy is of the order of $\pm 0{\cdot}03$ per cent sulphur for distillates and $\pm 0{\cdot}1$ per cent sulphur for crude oils and residual fuels. Details are given of the principle of the method, the equipment required, and the procedures for calibration and operation of the instrument. Experimental results are given which show the repeatability of the method, its absolute accuracy, and a comparison between such results and those obtained by conventional methods.

INTRODUCTION

LARGE numbers of determinations of total sulphur contents are required daily on a wide range of intermediate and final products in the normal operation of a refinery. The accuracy required is often not as high as that provided by conventional methods (for example the lamp method IP 107) and a method of lower but sufficient accuracy would be acceptable. In the control of refinery processes much of the value of the information given by conventional methods is lost on account of the delay in obtaining results, amounting to several hours and sometimes a day or more. The present method was developed in order to overcome these difficulties, and gives results simply and very speedily, with moderate accuracy.

Sullivan and Friedman in 1946 [1] described an X-ray absorption method for the quantitative analysis of lead in gasoline, and equipment was available commercially for this purpose shortly afterwards. Calculations showed that it would be practicable to apply an X-ray absorption method to the determination of sulphur in hydrocarbons and that good accuracy should be attainable in this way. A development programme was therefore put in hand, with the result that the present prototype equipment has been constructed. Parallel developments of the X-ray absorption method have taken place in the U.S.A., where it is now widely used for sulphur determination. For further information on the investigations of other workers in this field, reference should be made to an annual review of the published literature by Liebhafsky.[2] This paper is concerned with the Sunbury equipment, particular emphasis being laid on its capabilities and its applications, especially to the petroleum industry. A detailed description of the mechanical and electrical construction of the instrument will appear elsewhere in the literature.

PRINCIPLE OF THE METHOD

The absorption of X-rays by a material is a function of the numbers and kinds of atoms present, and is independent of their physical and chemical states. In general, the absorption per atom (and per unit mass) increases rapidly with atomic number. Hydrogen and carbon have atomic numbers of 1 and 6 respectively, while sulphur has an atomic number of 16. Sulphur can therefore be readily detected and estimated in the presence of hydrocarbons. Similarly, any other single element of high atomic number can be detected and estimated in an otherwise pure hydrocarbon.

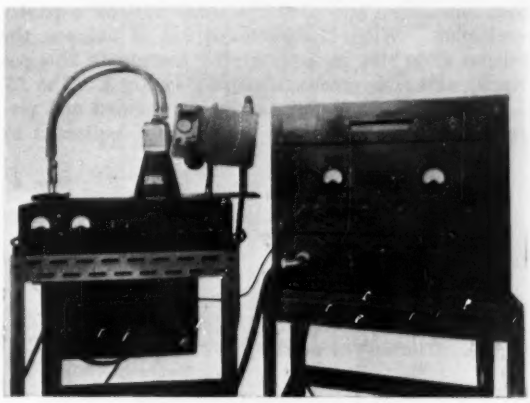

FIG 1
THE ABSORPTION UNIT

The equipment is shown in Fig 1. Two beams of X-rays 1 and 2, are passed through the unknown and a standard hydrocarbon respectively, as shown in Fig 2. The intensities falling on the fluorescent screens are equalized by adjusting the angle of tilt θ of a calibrated attenuator in the beam which passes through the unknown cell; the proportion of the X-ray intensity absorbed by the adjustable attenuator varies with the path length through it, and this in turn is proportional to sec θ. One of a series of standard attenuators, the choice of which depends on the approximate sulphur content of the sample, is inserted in the second X-ray

* MS received 2 October 1953.

beam, where it remains fixed in position. Thus at balance the position of the variable attenuator gives a measure of the difference in absorptive power between the unknown and standard cells, and hence a measure of the sulphur content of the unknown.

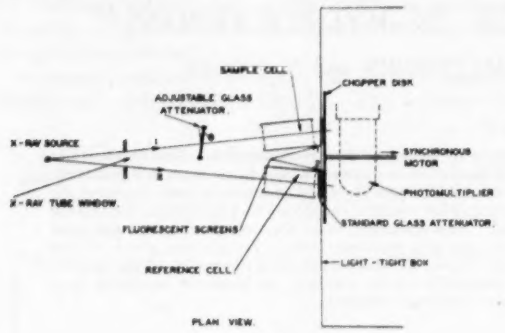

FIG 2

DIAGRAM OF THE ABSORPTION UNIT

The balance point is detected by allowing the two beams to fall on similar fluorescent screens. The light from these is chopped at 25 c.p.s., so that light from first one screen and then the other falls on a photomultiplier. When the instrument is off balance, the output from this photomultiplier contains a 25-c.p.s. ripple, and is as shown (idealized) in Fig 3. The 25-c.p.s. component in the output is amplified and presented on a galvanometer. Balance is indicated by the absence of 25-c.p.s. ripple, and hence by a nul deflection on the galvanometer.

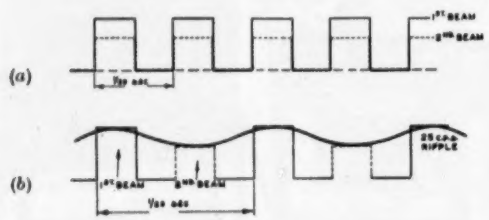

FIG 3

IDEALIZED WAVE-FORM OF THE PHOTOMULTIPLIER OUTPUT CURRENT

(*a*) Off balance output with no chopper. (*b*) Off balance output with 25-c.p.s. chopper.

EQUIPMENT

The equipment consists of three basic parts as shown in Fig 1, namely a source of X-rays, the absorption unit, and the amplifier. In addition, a voltage stabilizer is required in series with the mains supply to the equipment.

X-ray Source

The Philips (Eindhoven) X-ray set (type 11704) is shown on the left-hand side of Fig 1. The model was chosen primarily on account of its compact nature and simplicity of operation. Present experience confirms that the set is suited to the purpose required.

Absorption Unit

The principles of operation of the absorption unit have already been given. The following details are also of interest :

The normal sample cells are constructed in stainless steel and have capacities of about 5 ml (Fig 4). Cells of 2 ml capacity are available for small samples, and special cells are available for fuel oils and other viscous samples. The lithium fluoride end plates are held in position by screw caps, and each cell contains two holes for filling purposes, which are sealed during use with tapered plugs. The cells fit into a holder which can be located precisely in the apparatus and held in position by means of a knurled screw. The cell holder serves also as a constant temperature jacket, compressed air from the laboratory supply being circulated to keep its temperature constant to within $\pm 2^\circ$ C.

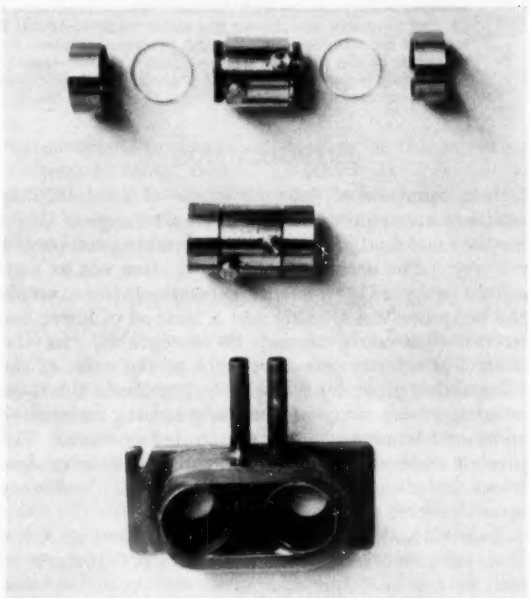

FIG 4

SAMPLE CELLS AND CELL HOLDER

Amplifier

The photomultiplier output is fed to an electronic circuit housed separately and shown on the right-hand side of Fig 1. The principal function of the circuit is to select and amplify any 25-c.p.s. component in the photomultiplier output and to present it on a microammeter or galvanometer. Coarse adjustment of balance is carried out by reference to a centre-zero microammeter and fine adjustment by switching the

galvanometer into circuit. The " amplifier " unit also contains a 700-volt D.C. power supply for the photomultiplier and a circuit, working in conjunction with an auxiliary motor and commutator in the housing of the absorption unit, to bring the chopper into the correct phase with respect to the mains voltage and the X-ray output. A block diagram of the electrical circuit is shown in Fig 5.

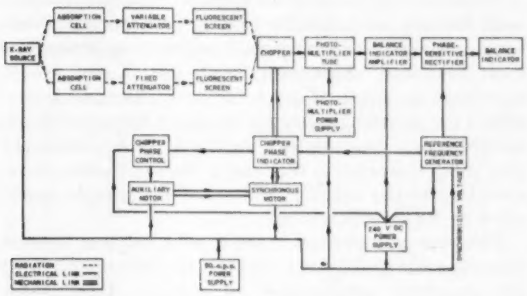

FIG 5

APPARATUS FOR SULPHUR ESTIMATION BY X-RAY ABSORPTION
BLOCK DIAGRAM

CALIBRATION

Since the absorption of X-rays by a sample depends on the numbers of atoms of each element present in the X-ray beam, it is clear that experimental results on petroleum fractions will in general be influenced by the following properties of the sample :

(*a*) the sulphur content ;
(*b*) the density ;
(*c*) the carbon : hydrogen ratio ; and
(*d*) the presence of elements other than carbon, hydrogen, and sulphur.

Experience has shown that item (*d*) causes negligible errors in determined sulphur contents for the whole range of distillate fractions and causes only small errors for crude oils and residues. The matter is discussed more fully in a later section.

The effect of variations in carbon : hydrogen ratio from sample to sample in introducing errors into the determined sulphur contents, can be reduced to negligible proportions by choosing to work at an effective X-ray wavelength as close as possible to that wavelength at which carbon and hydrogen have equal mass absorption coefficients.

Fig 6 shows the absorption coefficients of various elements per unit mass, plotted as functions of wavelength from published data.[3, 4, 5] It will be seen that carbon and hydrogen have equal mass absorption coefficients at a wavelength of 0·6 Å approximately, and that of sulphur is fourteen times as great at this wavelength. In order to minimize unwanted effects due to differences in carbon : hydrogen ratio in unknown samples, it is therefore desirable to work with an effective X-ray wavelength as close to 0·6 Å as possible. The relationship between kilovoltage and effective wavelength is complex and unknown, so that this optimum wavelength must be determined empirically. The procedure is as follows :

Two pure hydrocarbons of approximately equal hydrogen : carbon ratio and widely different but known densities are inserted in turn as unknown samples in the apparatus, and the absorption values are measured in terms of sec θ, as discussed later. These are plotted against the respective specific gravities, so giving a specific gravity calibration line for the particular hydrogen : carbon ratio. A third pure hydrocarbon of quite different hydrogen : carbon ratio is then measured, and the sec θ value is plotted against specific gravity on the same graph. In general, the new point will not lie on the earlier line, but in the case of a lower hydrogen : carbon ratio will lie above the line at too high kilovoltages and below it at too low kilovoltages ; in the case of a higher hydrogen : carbon ratio, the opposite state of affairs exists. The object is therefore to determine the kilovoltage at which the third point lies on the line through the first two points. The effective wavelength of the X-ray beam at this kilovoltage is then approximately 0·6 Å.

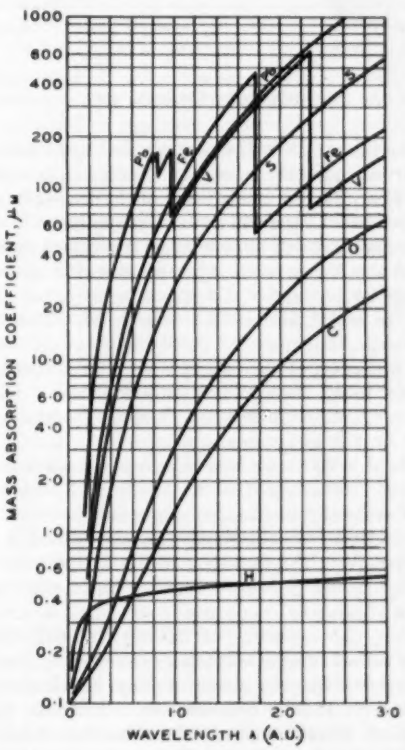

FIG 6

VARIATION OF MASS ABSORPTION COEFFICIENTS WITH
WAVELENGTH FOR VARIOUS ELEMENTS

Fig 7 shows the values of sec θ obtained for benzene, decalin, and methyl *cyclo*hexane for three different kilovoltage settings. The benzene point approaches the line as the kilovoltage is lowered, but does not reach the line at 38 kV, which is the lowest potential that can conveniently be used. The errors introduced in practice due to variations of hydrogen : carbon ratio when working at 38 kV are negligible.

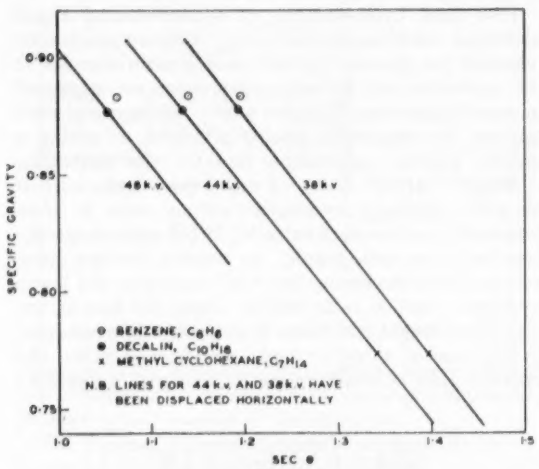

FIG 7

EFFECT OF VARYING THE H–C RATIO AT DIFFERENT KILOVOLTAGES (PHILIPS' SET)

Experiments have shown that the effective wavelength of the X-ray beam is not measurably altered by changing the material of the target from copper (Kα = 1·54 Å) to molybdenum (Kα = 0·71 Å). This result is to be expected, since the total energy of the characteristic radiation of the target is very small compared with the total energy contained in the "white" radiation (dependent only on X-ray-tube kilovoltage and not on the target material).

Effects due to variations in sample density can be eliminated, according to some authors,[6] by operating with a fixed weight of sample rather than with a fixed volume. However, the fixed volume method is more convenient from the experimental point of view, and is utilized in the present method. Since the specific gravities of samples are normally measured as a matter of routine, the necessity of having this information requires no additional experimental work. For present purposes specific gravities may be obtained by hydrometer. It is unnecessary to convert the figures to densities, provided the calibrations have also been made in terms of specific gravity.

The basic equation for the calculation of sulphur contents, derived in the Appendix, is :

$$x = K\frac{\sec\theta_{HC} - \sec\theta_S}{\rho_1} \quad . \quad . \quad . \quad . \quad (1)$$

where x is weight per cent of sulphur, θ_S is the angle of inclination of the attenuator at the balance point for the sample, θ_{HC} is the angle of inclination of the attenuator at the balance point for a sulphur-free sample of equal specific gravity, ρ_1 is the sample specific gravity, and K is a calibration constant.

Thus the X-ray results, expressed in terms of sec θ, vary linearly with specific gravity for pure hydrocarbons. A specific gravity calibration is produced for each standard attenuator, and the X-ray result, expressed in terms of sec θ for every sample, is corrected for specific gravity by means of the appropriate calibration in the manner indicated in equation (1). The value corrected in this way is the sec θ value corresponding to the sulphur content of the sample multiplied by its specific gravity.

The rate of variation of sec θ with sulphur content times specific gravity is found not to differ appreciably for standard attenuators of various thicknesses. (Theoretically the rates should alter with increasing thickness of standard attenuator, since the latter has the effect of modifying the effective wavelength of the X-ray beam.) It is therefore convenient and sufficiently accurate for present purposes to assume that the percentage sulphur times specific gravity calibration is in fact the same for all the standard attenuators. Separate specific gravity calibration lines must, however, be plotted for each standard attenuator.

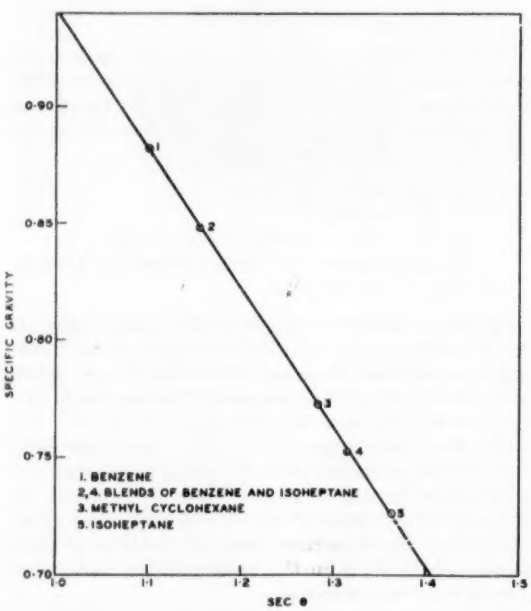

FIG 8

TYPICAL CALIBRATION. SEC θ VS. SPECIFIC GRAVITY FOR A PARTICULAR STANDARD ATTENUATOR

A typical specific gravity calibration for one of the standard attenuators is shown in Fig 8. As predicted by equation (1), there is clearly a linear relationship between sec θ and specific gravity for zero sulphur

content. Fig 9 shows the calibration line for sec θ corrected for specific gravity in terms of percentage sulphur content times specific gravity. Fig 9 and the specific-gravity calibrations for the standard attenuators have been obtained using a series of seventeen blends representing sulphur contents varying between zero and 4 per cent and specific gravities of approxi-

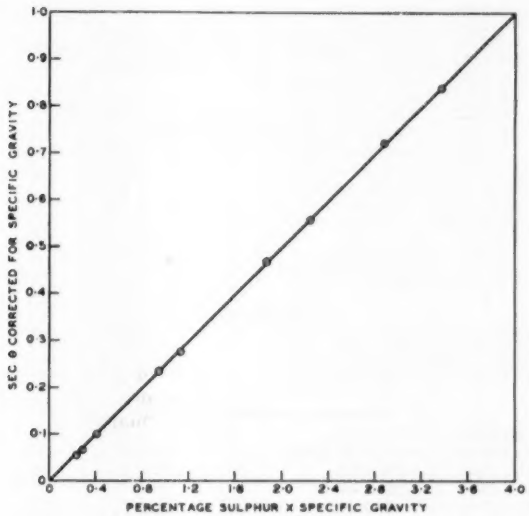

FIG 9

CALIBRATION. SEC θ CORRECTED FOR SPECIFIC GRAVITY VS. PERCENTAGE SULPHUR × SPECIFIC GRAVITY FOR ALL STANDARD ATTENUATORS

mately 0·75 and 0·90. The sulphur contents on which the calibrations are based were determined by the Lamp Method.

OPERATION

The procedure for measuring the X-ray absorption of a sample is as follows : The amplifier is switched on and allowed to warm up for ½ hr before any measurements are taken. The sample cell is placed in a jig and filled with the sample to be measured, care being taken to eliminate air bubbles. The reference cell, containing a suitable hydrocarbon, *e.g.*, methyl *cyclo*-hexane, and the sample cell are placed in the cell holder which is inserted in the absorption unit (see Fig 4). One of a series of standard attenuators is inserted, depending on the expected sulphur level of the sample. The X-ray set is switched on and brought to the correct working potential of 38 kV peak. The attenuator handle is turned until approximate balance is indicated by the right-hand meter (Fig 1); the galvanometer is then switched into circuit, the instrument is balanced accurately and the attenuator reading is taken. By referring to a calibration table, the value of sec θ corresponding to the dial reading is obtained directly. The galvanometer and the X-rays are switched off, and the sample cell is removed and cleaned ready for the next sample. The whole cycle of operations takes approximately 5 minutes.

Drifts occur in the X-ray measurements from time to time, particularly during the warming-up period. However, by inserting a check cell as a matter of routine after every three or four unknowns, allowance can be made for any slight drifts. Stray results have been found to occur very occasionally, and since the above procedure offers no check on such strays, determinations are made in duplicate whenever possible. Provided duplicate results lie within the repeatability of the method, their average is reported.

EXPERIMENTAL RESULTS

(a) *Assessment of Repeatability*

Repeatability is normally assessed on independent results obtained under conditions giving a high degree of correlation, *i.e.*, on results obtained over a short period of time. Under these conditions the repeatability of the X-ray method is better than 0·02 per cent. A more useful figure is the " repeatability " of results widely spaced in time, *i.e.*, " reproducibility " for a single apparatus. This figure is derived below.

A large number of routine samples and blends have been analysed in replicate by the X-ray method. In most cases replicate determinations have been carried out at widely spaced times and usually on different days. Table I gives a complete list of results from which the repeatability has been calculated. Owing to minor variations in technique it is not certain that the single determinations of some of the sets of replicates are strictly comparable, but to avoid any arbitrary selection of results the full set is given. The true repeatability is therefore not worse than, and is probably better than, the calculated repeatability of the method. The following results have been calculated by the normal statistical procedure.[7]

Duplicate determinations carried out at widely separated times or on different days differ by 0·07 per cent weight of sulphur or less in 95 per cent cases. This figure applies equally to distillates and residual fuels. If duplicate determinations are carried out, as is recommended, the means have 95 per cent confidence limits of $\pm 0{\cdot}035$ per cent weight of sulphur.

(b) *Assessment of Absolute Accuracy*

Accurately prepared synthetic blends are the primary standards against which all methods for determining sulphur contents are ultimately assessed. Two series of blends were therefore made up with the highest possible degree of accuracy, special care having been taken to minimize evaporation errors. The first series was prepared by dissolving elemental sulphur in xylene (A.R. grade, originally thought to be sulphur-free but since found to contain 0·06 per cent sulphur) in various concentrations. The second series was prepared by dissolving *n*-propyl sulphide in *iso*-octane. The *n*-propyl sulphide was assumed to be pure, but

TABLE I

Replicate Determinations on Routine Samples and Blends

Sample identification	Results of single X-ray determinations
	Gas Oils
H.5853	0·39, 0·40, 0·39
H.5890	0·26, 0·25
H.7439	0·41, 0·46, 0·45, 0·48
H.7473	0·64, 0·64, 0·64
H.7488	0·29, 0·31
H.7597	0·59, 0·68, 0·69, 0·63, 0·60, 0·63, 0·66
H.7598	0·64, 0·71, 0·68
H.7599	0·41, 0·46
H.7620	0·07, 0·06
H.7637	0·36, 0·37
H.7672	0·09, 0·09
H.7673	0·09, 0·14, 0·13
H.7686	0·57, 0·53
H.7688	0·39, 0·42, 0·42, 0·45
H.7680	0·10, 0·15
H.7682	0·19, 0·24
H.7684	0·32, 0·34
H.7687	0·65, 0·60
H.7701	0·39, 0·39
H.7702	0·42, 0·42
H.8151	0·14, 0·11
H.8170	0·39, 0·42
H.8176	0·62, 0·63, 0·60
H.8173	0·36, 0·35, 0·34, 0·36, 0·33
H.8193	0·17, 0·16
H.8194	0·33, 0·33
H.8205	0·06, 0·06
H.8206	0·03, 0·04
H.8207	0·07, 0·08
H.8208	0·15, 0·14
H.8209	0·41, 0·41
H.8210	0·46, 0·45
H.8220	0·62, 0·57
H.8221	0·25, 0·22
H.8429	0·20, 0·21, 0·19, 0·22, 0·22, 0·20, 0·22, 0·21
H.8698	0·72, 0·69, 0·71
H.8733	1·18, 1·16, 1·13, 1·12, 1·14
H.8772	0·43, 0·45
H.8773	0·54, 0·54
H.8774	0·59, 0·61
H.8775	0·35, 0·37
H.8782	0·05, 0·05
H.8715	0·09, 0·07
H.8716	0·42, 0·45
H.8857	0·13, 0·15, 0·13
H.8859	0·18, 0·20, 0·20
H.8864	0·09, 0·10, 0·11, 0·03, 0·04, 0·04
H.8865	0·05, 0·05, 0·09, 0·14, 0·15
H.8868	0·07, 0·05, 0·12, 0·10
H.8869	0·04, 0·04, 0·09, 0·10
H.8870	0·10, 0·13, 0·16, 0·19
H.8885	0·36, 0·36
H.8911	0·08, 0·07
H.8912	0·04, 0·07
H.8913	0·43, 0·42
H.9047	1·25, 1·22
H.9048	0·21, 0·26
H.9049	0·36, 0·37
H.9053	0·41, 0·43
H.9058	1·39, 1·38
H.9127	1·21, 1·24
H.9160	1·37, 1·37
	Gas Oils (continued)
H.9245	1·24, 1·25
H.9246	0·20, 0·19
H.9285	0·16, 0·17
H.9286	0·24, 0·28
H.9288	0·55, 0·48, 0·49
H.9291	0·20, 0·17
H.9492	0·14, 0·09, 0·15
H.9475	0·31, 0·33
F.1482	0·50, 0·49, 0·49
F.1489	0·43, 0·44, 0·43, 0·43, 0·42, 0·40
F.1498	0·46, 0·45, 0·44
B.52/472	1·00, 0·94
B.52/476	0·90, 0·92, 0·94
B.52/492	0·91, 0·95
B.52/556	1·48, 1·50, 1·51
G.0.7	0·44, 0·45
G.0.8	0·51, 0·49
G.0.9	0·50, 0·52
	Gasolines
W51/627	0·30, 0·29
DHN/437A	0·20, 0·22
D.2778/9	0·04, 0·03
	Kerosines (including A.T.F.)
RG.2659	0·17, 0·18
RG.3663	0·34, 0·35, 0·39
RG.3664	0·30, 0·30
RG.3811	0·38, 0·37
RG.3812	0·41, 0·44
RG.3813	0·10, 0·14, 0·15
RG.3814	0·47, 0·47
PD1217/2	0·20, 0·19
W52/1902	0·05, 0·06
W52/1903	0·03, 0·05, 0·05
W52/1904	0·02, 0·02
LO/125	0, 0·01
	Fuel Oils
9006	2·94, 2·98, 2·96
9007	2·05, 2·08, 2·05
9008	2·01, 2·04, 1·99
9010	2·08, 2·08, 2·00
9121	2·27, 2·32
9255	2·40, 2·38, 2·40
9258	1·06, 1·13
9259	1·11, 1·05, 1·08
15104	2·89, 2·94, 2·92, 2·94
15352	2·33, 2·36
15591	2·67, 2·67
	Synthetic Blends in Sulphur-free Solvents
3	1·28, 1·25, 1·29, 1·29, 1·33, 1·23, 1·29, 1·28
4	2·52, 2·51, 2·55, 2·55, 2·50, 2·55, 2·50, 2·55, 2·58
7	1·22, 1·28, 1·20, 1·27, 1·24, 1·29, 1·22, 1·24, 1·21
8	0·31, 0·31, 0·30, 0·31, 0·29, 0·30
10	0·30, 0·31, 0·30
14	2·53, 2·60, 2·60, 2·55, 2·50, 2·54, 2·53, 2·49
25	3·75, 3·64, 3·73, 3·71, 3·75, 3·80
64	3·87, 3·91, 3·84, 3·89, 3·85, 3·99
"B"	0·49, 0·49, 0·50, 0·51, 0·48, 0·49, 0·49, etc.

has since been found to be 97 per cent pure. The X-ray results on both series were obtained in one day. Results on the two series are compatible and show that for the conditions under which the results were obtained, single X-ray results differ from the theoretical blend figures by 0·015 per cent weight of sulphur or less in 95 per cent cases. This figure of 0·015 per cent approximates to the X-ray repeatability over a short period of time.

(c) *Comparison of Results by the X-ray Method with those by Conventional Methods*

Sulphur contents of a large number of routine samples of all types have been determined both by

the X-ray method and by conventional methods (lamp or bomb) to provide data for a comparison of the methods.

TABLE II

Comparison of Results by X-ray Method and by Conventional Methods

Sample	% S by X-ray method	% S by conventional method	Difference
Gas Oils (X-ray v. lamp results)			
5622	0·07	0·05	0·02
5651	0·18	0·18	0
5668	0·04	0·02	0·02
5678	0·13	0·15	0·02
5853	0·39	0·38	0·01
5870	0·08	0·07	0·01
5873	0·25	0·28	0·03
5875	0·30	0·35	0·05
5878	0·82	0·92	0·10
5879	0·08	0·07	0·01
5880	0·13	0·12	0·01
5881	0·18	0·17	0·01
5887	0·23	0·22	0·01
5890	0·25	0·23	0·02
5893	0·28	0·29	0·01
7439	0·45	0·48	0·03
7463	0·15	0·16	0·01
7473	0·64	0·64	0
7483	0·07	0·10	0·03
7485	0·21	0·24	0·03
7488	0·30	0·33	0·03
7489	0·33	0·34	0·01
7490	0·35	0·39	0·04
7593	0·36	0·38	0·02
7596	0·19	0·19	0
7597	0·64	0·66	0·02
7598	0·68	0·71	0·03
7599	0·44	0·46	0·02
7616	0·30	0·31	0·01
7620	0·06	0·05	0·01
7622	0·27	0·29	0·02
7623	0·37	0·38	0·01
7631	0·41	0·38	0·03
7632	0·48	0·50	0·02
7637	0·37	0·37	0
7640	0·01	0·01	0
7641	0·02	0·01	0·01
7642	0·54	0·55	0·01
7650	0·06	0·01	0·05
7672	0·09	0·05	0·04
7673	0·12	0·10	0·02
7674	0·43	0·43	0
7676	0·38	0·37	0·01
7677	0·40	0·41	0·01
7679	0·10	0·06	0·04
7680	0·13	0·09	0·04
7681	0·15	0·09	0·06
7682	0·22	0·17	0·05
7683	0·24	0·25	0·01
7684	0·33	0·32	0·01
7685	0·46	0·53	0·07
7686	0·55	0·58	0·03
7687	0·62	0·55	0·07
7688	0·42	0·44	0·02
7689	0·46	0·49	0·03
7690	0·46	0·53	0·07
7693	0·14	0·10	0·04
7696	0·62	0·70	0·08
7697	0·39	0·38	0·01
7701	0·39	0·38	0·01
7702	0·42	0·41	0·01
7742	0·36	0·37	0·01
8692	0·29	0·29	0
8693	0·60	0·64	0·04
8694	0·66	0·69	0·03
8698	0·69	0·71	0·02
8705	0·46	0·44	0·02
8734	0·40	0·39	0·01
9291	0·17	0·12	0·05
9297	0·16	0·16	0
9311	0·38	0·32	0·06
9325	0·18	0·10	0·08
9371D	1·98	1·91	0·07
9475	0·32	0·27	0·05
F/1412	0·38	0·41	0·03
F/1757	0·96	0·99	0·03
S01	0·05	0·02	0·03
S06	0·67	0·74	0·07
B/51/156	0·07	0·03	0·04
Gasolines (X-ray v. lamp results)			
W51/367	0·02	0·02	0
W51/415	0·42	0·41	0·01
W51/438	0·05	0·01	0·04
W51/625	0·09	0·07	0·02
W51/627	0·29	0·29	0
DHN/429A	0·14	0·14	0
DHN/437A	0·21	0·20	0·01
D2778/9	0·03	0·004	0·03
ED1	0·02	0·001	0·02
Kerosines (X-ray v. lamp results)			
W51/370	0·20	0·17	0·03
W51/660	0·23	0·25	0·02
RG.2659	0·17	0·17	0
RG.3877	0·37	0·29	0·08
RG.3878	0·28	0·29	0·01
H.9294	0·14	0·13	0·01
H.9314	0·14	0·13	0·01
EB241	0·20	0·22	0·02
PD1217/2	0·19	0·14	0·05
D2778/13	0·50	0·50	0
Vaporizing Oils (X-ray v. lamp results)			
B.51/184	0·21	0·23	0·02
B.51/185	0·10	0·12	0·02
Lubricating Oils (X-ray v. bomb results)			
L51/246	0·37	0·34	0·03
L52/307	1·36	1·42	0·06
L52/312	1·25	1·31	0·06
L52/348	0·66	0·58	0·08
R.760	1·22	1·29	0·07
R.762	1·42	1·34	0·08
301	2·55	2·65	0·10
360	1·87	1·76	0·09
4147	1·82	1·84	0·02
4148	2·22	2·32	0·10
5872	2·07	2·10	0·03
5873	1·98	1·98	0
5874	1·95	1·94	0·01
5876	1·76	1·79	0·03
6399	0·89	0·93	0·04
Fuel Oils (X-ray v. bomb results)			
B.52/525	1·43	1·36	0·07
B.52/561	2·48	2·64	0·16
B.52/566	3·06	3·15	0·09
B.3/86	1·41	1·42	0·01
B.3/87	1·40	1·43	0·03
B.3/88	1·38	1·39	0·01
B.3/131	1·86	1·83	0·03
B.3/132	2·14	2·18	0·04
B.3/133	3·01	3·10	0·09
B.3/134	3·25	3·37	0·12
9006	2·96	2·89	0·07
9007	2·06	1·86	0·20
9008	2·01	1·93	0·08
9010	2·05	1·96	0·09
9121	2·29	2·25	0·04
9123	3·22	3·23	0·01
9255	2·39	2·39	0
9258	1·10	1·22	0·12
9259	1·08	1·21	0·13
15104	2·92	2·95	0·03
15350	3·21	3·26	0·05
15352	2·34	2·19	0·15
15591	2·67	2·66	0·01
15865	2·41	2·34	0·07
Crude Oils (X-ray v. lamp results)			
B2558	1·23	1·27	0·04
Synthetic Blends (X-ray v. lamp results)			
3	1·28	1·29	0·01
4	2·53	2·52	0·01
7	1·24	1·28	0·04
8	0·31	0·34	0·03
10	0·30	0·34	0·04
13	0·49	0·49	0
14	2·54	2·50	0·04
25	3·73	3·73	0
64	3·84	3·81	0·03

Mean results on each sample are listed in Table II. The agreement is as follows:

Distillates:

Difference between results by X-ray and lamp methods, %	Percentage of total samples examined
0·01 or less	41
0·02 ,,	60
0·03 ,,	75
0·04 ,,	83
0·05 ,,	89

Fuel Oils and Residues:

Difference between results by X-ray and bomb methods, %	Percentage of total samples examined
0·04 or less	38
0·01 ,,	76
0·15 ,,	92
0·20 ,,	100

The errors may be attributed either to the X-ray method, or to the conventional method, or partly to each. In the cases of fuel oils and residues it is known that part of the error lies with the X-ray method which gives slightly high results for hydrocarbons containing trace elements of high atomic number. It is to be

TABLE III

The Theoretical Effect of the Presence of Other Elements on Accuracy for a Wavelength of 0·71 Å *

Element	Atomic number	Mass absorption coefficient	P.p.m. by wt on crude (maximum)	Sulphur estimate high by amount: approx wt %
Al	13	5·30	10	0·001
Ca	20	19·8	2 (mean)	0·0005
			40 (max)	0·01
Cr	24	30·4	0·5	0·0002
Co	27	41·6	10	0·004
Cu	29	49·7	10	0·006
Fe	26	38·3	4 (mean)	0·002
			90 (max)	0·04
Mg	12	4·38	80	0·003
Mn	25	33·5	0	0
Mo	42	20·2	1·0	0·0001
Ni	28	47·4	5 (mean)	0·004
			40 (max)	0·025
Pb	82	141	5	0·0004
Si	14	6·70	10	0·001
Na	11	3·36	80	0·0026
Sn	50	33·3	1·0	0·0003
Ti	22	23·7	5·0	0·0015
V	23	26·5	15 (mean)	0·04
			80 (max)	0·2
Zn	30	54·8	10	0·005

* Calculated for Mo Kα radiation, $\lambda = 0{\cdot}71$ Å.

For $\lambda = 0{\cdot}60$ Å, the figures in the right-hand column will not be changed appreciably, except in the case of molybdenum, where the new figure will read 0·001 approximately (molybdenum has its K absorption edge between the two wavelengths concerned, at 0·62 Å).

N.B.—This table has been computed for crude oils. For fuel oils the errors introduced may be taken as approximately twice as great on the average as the figures indicated.

emphasized that no corrections have been applied to the results in respect of the average metallic contents of the fuels. In order to estimate the expected magnitude of this error, data have been collected in Table III for the maximum contents of various trace elements in a wide range of crudes. Where the maximum content is abnormally high, the average content is also quoted. The theoretical error in measured sulphur content caused by the trace elements is shown in the last column of the table. The maximum amount by which the measured sulphur content of any crude is likely to be in error is 0·2 per cent sulphur, and an average value is likely to be 0·05 per cent for a crude containing 15 p.p.m. of vanadium. These errors always tend to make the sulphur estimate high.

DISCUSSION

With one operator, the average time for a single determination on a routine distillate sample is approximately 5 minutes, a considerable proportion of this time being taken up in loading, emptying, and cleaning the sample cell. Fifty single determinations or twenty-five determinations in duplicate can readily be carried out in an 8-hr day. For fuel oils the rate is slower than this on account of the longer time taken to empty and clean the cells. The time per sample varies between 5 minutes and 15 minutes, depending on the viscosity.

The accuracy is of the order of $\pm 0{\cdot}03$ per cent sulphur for distillates and $\pm 0{\cdot}1$ per cent sulphur for typical residual fuels and crude oils, and is sufficient for a large proportion of the determinations carried out daily in a petroleum inspection laboratory. On account of the rapidity with which results can be obtained, it is believed that the method will find wide application in the petroleum industry in process control and other work where speed is a factor of importance. Although the cost of the equipment is higher than that of the apparatus required for the conventional methods of sulphur determination, running costs are negligible, and it is considered that the equipment pays for itself in a few months by means of the man-hours saved per determination.

The instrument described can be applied without modification to the determination of tetra-ethyl lead in gasoline and with little or no modification to the determination of other additives in hydrocarbon fractions, such as lubricating oils. Other possible applications outside the petroleum industry are widespread, and include the determination of concentrations of salts of heavy metals in solutions and the total concentrations of suspended particles of known or constant compositions in liquid or gaseous media.

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APPENDIX

The equation giving the attenuation of a beam of X-rays of wavelength λ passing through matter is

$$I = I_0 e^{-\mu d} \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where I_0 is the incident X-ray intensity and I is the intensity of the emergent beam; d is the path length in the scattering material and μ is its volumetric absorption coefficient for rays of wavelength λ. μ is a function of wavelength and of the numbers and kinds of atoms present, but is independent of their states of chemical combination. Equation (1) is more conveniently written:

$$\log I_0 - \log I = \mu d \quad . \quad . \quad . \quad (2)$$

Let I_1 and I_2 be the intensities of X-rays of wavelength λ falling on the fluorescent screens 1 and 2 respectively (Fig 2) for an incident intensity I_0. Then the condition for balance is

$$I_1 = kI_2 \, . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

where the factor k, which is a constant for the instrument, is invoked to take account of slight inequalities between the two fluorescent screens and between the optical paths from the fluorescent screens to the photomultiplier etc.

I_1 and I_2 are given by equation (2), after allowance has been made for the absorbancies of the various materials present in the two beams, as follows:

$$\log I_0 - \log I_1 = \mu_t t_1 \sec \theta_S + \mu_p p_1 + (\mu_S x + \mu_H y_1 + \mu_C z_1)\rho_1 l_1 \quad (4)$$

$$\log I_0 - \log I_2 = \mu_p p_2 + (\mu_H y_2 + \mu_C z_2)\rho_2 l_2 + \mu_t t_2 \quad (5)$$

where μ_t is the absorption coefficient of the glass attenuators per unit thickness at wavelength λ, μ_p is the absorption coefficient of the lithium fluoride cell end plates per unit thickness at wavelength λ, μ_S is the absorption coefficient of sulphur per unit mass at

wavelength λ, μ_H is the absorption coefficient of hydrogen per unit mass at wavelength λ, μ_C is the absorption coefficient of carbon per unit mass at wavelength λ, t_1 is the path length through the variable attenuator when $\theta = 0$, t_2 is the path length through the standard attenuator, p_1 is the total thickness of the sample cell end plates, p_2 is the total thickness of the reference cell end plates, l_1 is the inside length of the sample cell, l_2 is the inside length of the reference cell, x is the proportion by weight of sulphur in the sample, y_1 is the proportion by weight of hydrogen in the sample, z_1 is the proportion by weight of carbon in the sample, y_2 is the proportion by weight of hydrogen in the reference hydrocarbon, z_2 is the proportion by weight of carbon in the reference hydrocarbon, ρ_1 is the density of the sample, ρ_2 is the density of the reference hydrocarbon, and θ_S is the angle of inclination of the variable attenuator (shown in Fig 2). By subtracting equation (4) from equation (5) and by substituting for I_1 from equation (3), the following equation is obtained for the condition at balance :

$$\mu_t t_1 \sec \theta_S + \mu_p p_1 + (\mu_S x + \mu_H y_1 + \mu_C z_1)\rho_1 l_1 = \mu_p p_2 + (\mu_H y_2 + \mu_C z_2)\rho_2 l_2 + \mu_t t_2 - \log k \quad (6)$$

The X-ray beam used in practice comprises a range of wavelengths so that the various absorption coefficients in equation (6) are mean values corresponding to the effective wavelength of the X-ray beam. The effective wavelength is a function mainly of the operating voltage of the X-ray tube and is chosen empirically so that μ_H and μ_C are as nearly as possible equal. Thus the effect of variations of carbon : hydrogen ratio from sample to sample on results is minimized and in practice is negligible. Equation (6) then becomes :

$$\mu_t t_1 \sec \theta_S + (\mu_S x + \mu_{HC}\overline{1 - x})\rho_1 l_1 = \mu_{HC}\rho_2 l_2 + \mu_t t_2 + \mu_p(p_2 - p_1) - \log k \quad (7)$$

The first term represents the absorption of the variable attenuator, the second term that of the sample, the third that of the reference sample, and the fourth that of the standard attenuator. The fifth term accounts for the absorptions of the various cell end plates and like the last term is a constant of the instrument.

The calibrations and subsequent measurements are based on a given hydrocarbon and reference cell, and separate calibration curves are determined on each of several standard attenuators (thicknesses t_2) covering the range of sulphur contents 0 to 4 per cent and densities 0·6 to 1·0 g/ml.

Thus for any given standard attenuator, we have for a sample at balance :

$$\mu_t t_1 \sec \theta_S + (\mu_S x + \mu_{HC}\overline{1 - x})\rho_1 l_1 = k' \quad (8)$$

The three variables in this equation under normal working conditions are x, ρ_1, and θ_S. In order to evaluate the sulphur content x in terms of the attenuator angle θ_S it is necessary to know the effect of the sample density ρ_1 on θ_S. This is found from the calibration curve of sec θ versus ρ for zero sulphur content, which then gives :

$$\mu_t t_1 \sec \theta_{HC} + \mu_{HC}\rho_1 l_1 = k' \quad . \quad . \quad (9)$$

Subtracting equation (8) from equation (9) then gives :

$$x = \frac{\mu_t t_1 (\sec \theta_{HC} - \sec \theta_S)}{\rho_1 l_1 (\mu_S - \mu_{HC})} = K\frac{\sec \theta_{HC} - \sec \theta_S}{\rho_1} \quad . \quad . \quad (10)$$

In practice it is more convenient to work in terms of specific gravity rather than density; the only effect on the above equation is to modify slightly the constant K. Equation (10) is then the basic equation by which sulphur contents are calculated from the experimental data.

DETERMINATION OF THE ASPHALTENES CONTENT OF BITUMEN

As a result of a co-operative programme of work in which five laboratories have participated, Standardization Sub-Committee No. 7 proposes to adopt IP 6/53, Asphaltenes in Oil, for use with bitumen. This method has the great advantage that it involves the use of a pure compound, *n*-heptane, as precipitant. The precision of the method when applied to bitumen has been shown to be satisfactory. It would follow with the acceptance of this proposal that the asphaltenes content of petroleum products generally would become " the percentage by weight of wax-free material insoluble in *n*-heptane but soluble in hot benzene." Previously, it has been necessary when determining the asphaltenes content of bitumen, to deduct from the percentage of material insoluble in IP Petroleum Spirit the amount of material insoluble in carbon disulphide, as determined on a separate portion of bitumen by method IP 47.

Comments on the suggested change will be welcomed by the Bitumen Sub-Committee, and should be addressed to the Technical Assistant of the Institute at an early date.

OBITUARY

C. H. BARTON

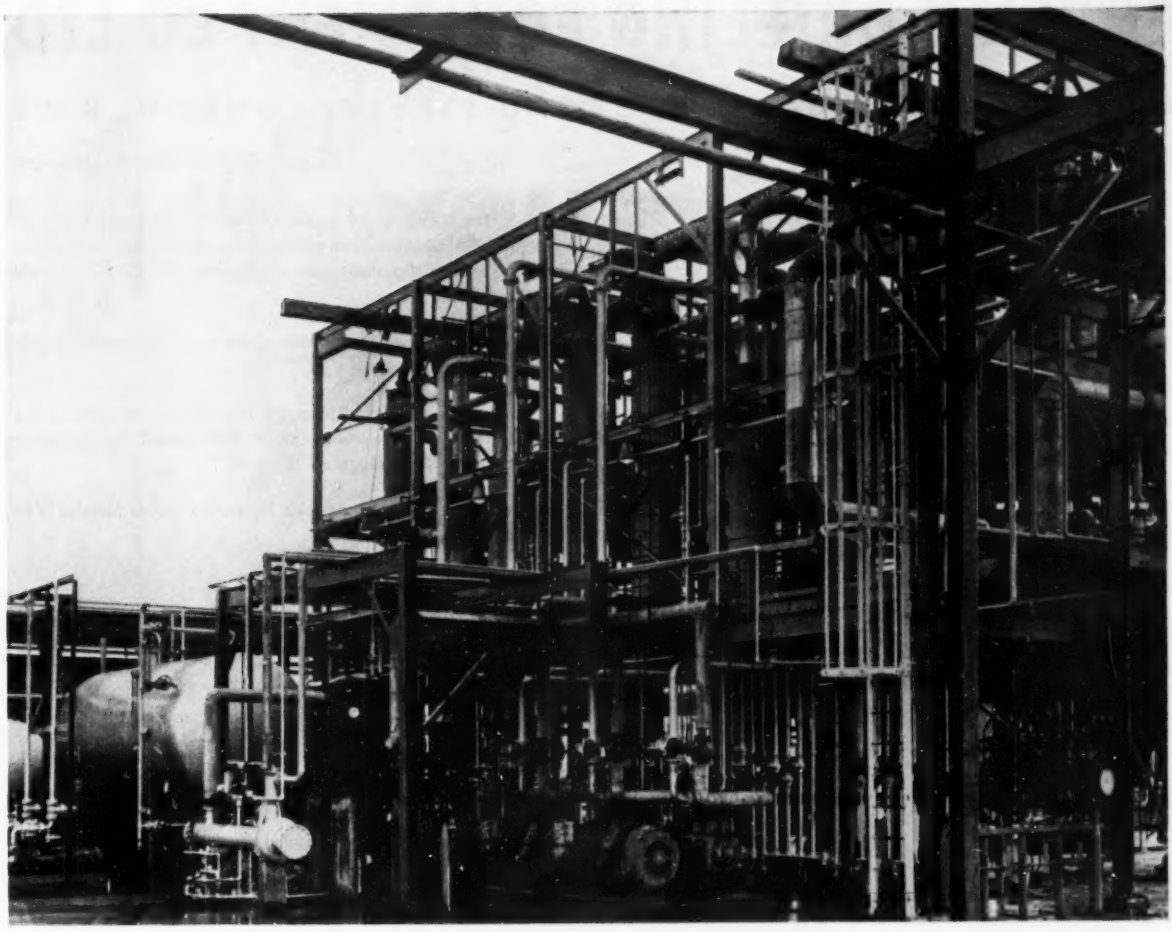
It was with deep regret that his friends in the U.K. learnt of the sudden death of Cyril Barton in the U.S.A. on 10 December 1953.

He was born on 4 September 1897 at Smethwick, Staffordshire. Educated at King Edward's School, Birmingham, he obtained an open scholarship to Jesus College, Cambridge, in 1916. He then joined the Army and served in Italy. On leaving the Army early in 1919, he went up to Cambridge, and would have sat for his Tripos in 1921 had it not been for an accident in the laboratory which affected his eyesight ever afterwards. He obtained a First Class in Chemistry in Part II of the Natural Science Tripos in 1922.

After graduation he joined the laboratory of the Anglo-Mexican Petroleum Co., where he worked with A. G. Marshall, who was then engaged on research on lubricating oils. When Marshall left for the U.S.A. in 1926, Cyril Barton took over this work and joined the Chemical Department of the Asiatic Petroleum Co. He was particularly concerned with engine research on motor fuels and lubricants, in close association with Messrs. Ricardo's. In this field he became a recognized expert and published a considerable number of papers. He was elected a member of the Institute of Petroleum in 1931, transferring to Fellow in 1938. During the war he was actively concerned with the examination of samples of enemy fuels and lubricants for determining their origin. In 1945 he was transferred to the Products Application Department of the Shell Oil Inc. in New York, and remained there until his death.

Cyril Barton had an enormous capacity for work. His quiet manner was deceptive and concealed a character of no little determination, and he had a very lively sense of humour. A keen and sensitive musician, he was a pianist of more than average attainments. His passing has left a great sense of loss among his many friends in various parts of the world, and they offer their heartfelt sympathies to his widow and young son.

F. L. G.



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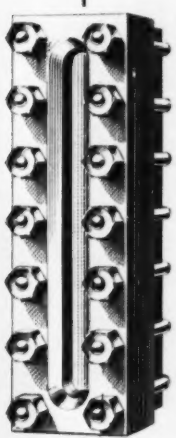

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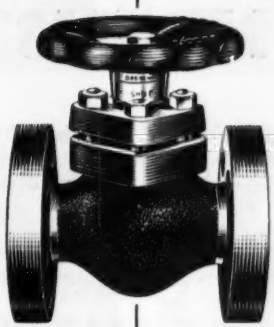

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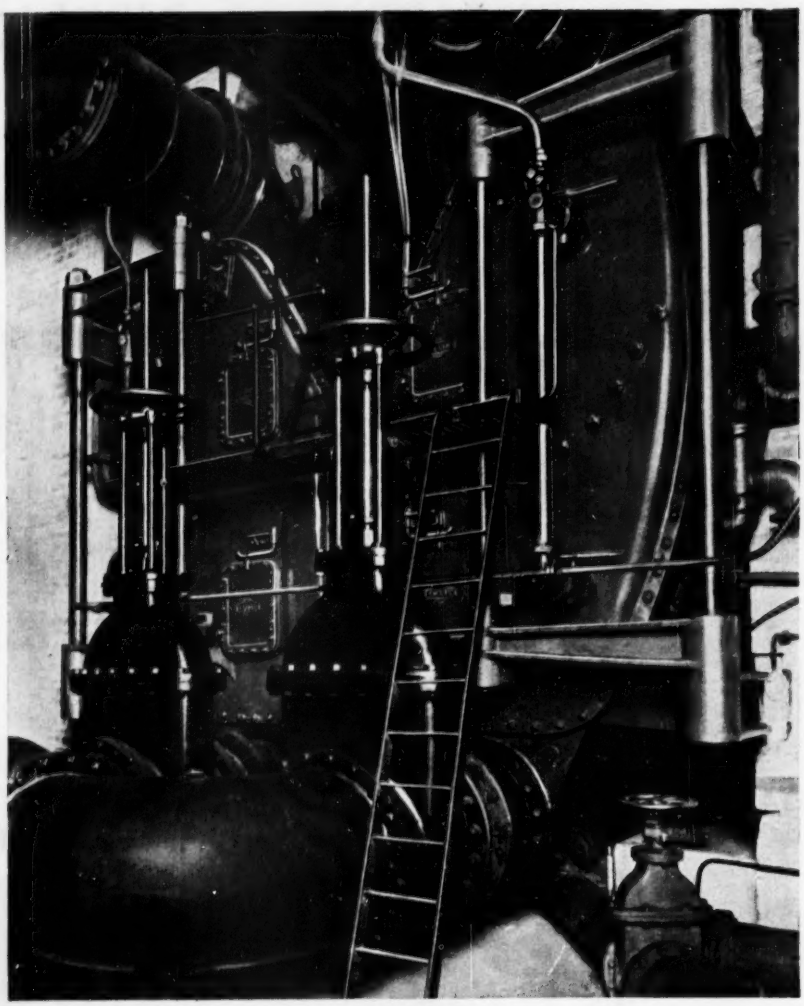

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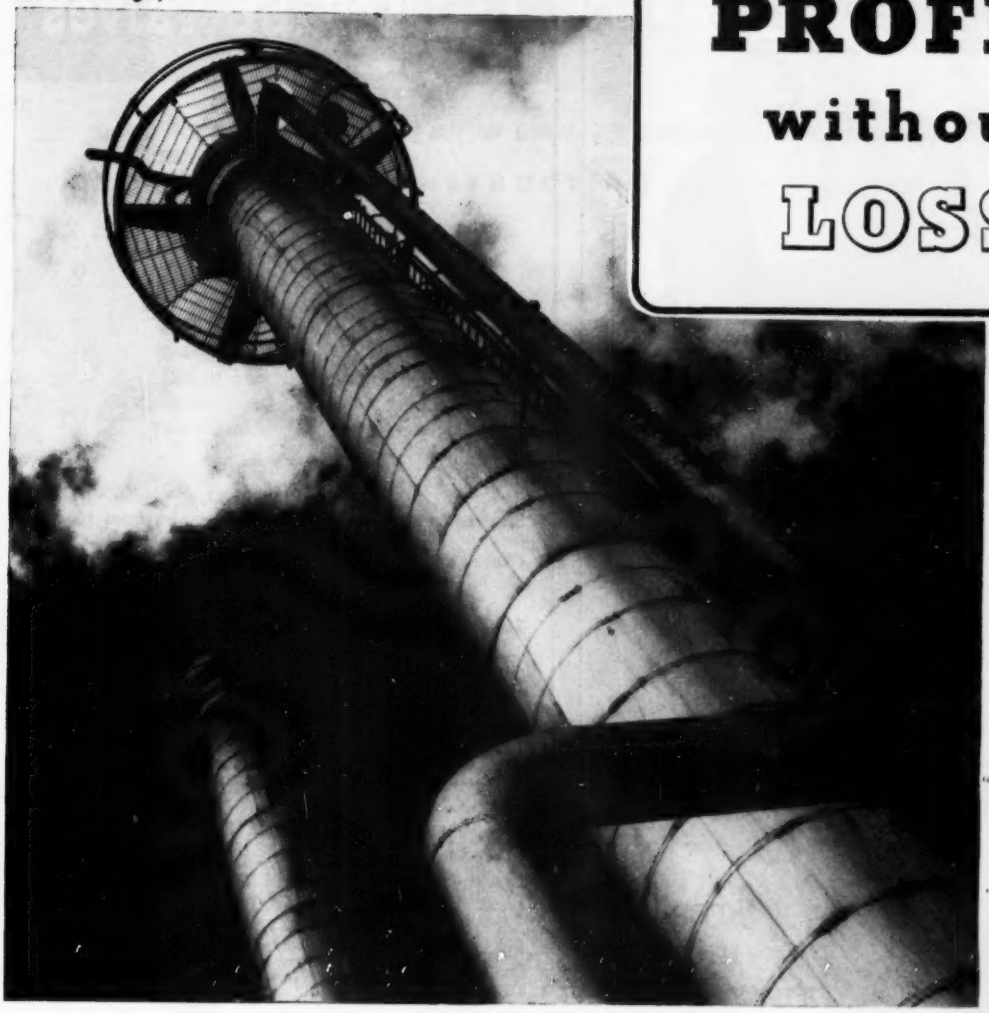

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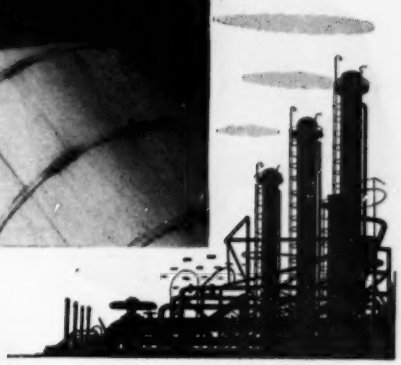

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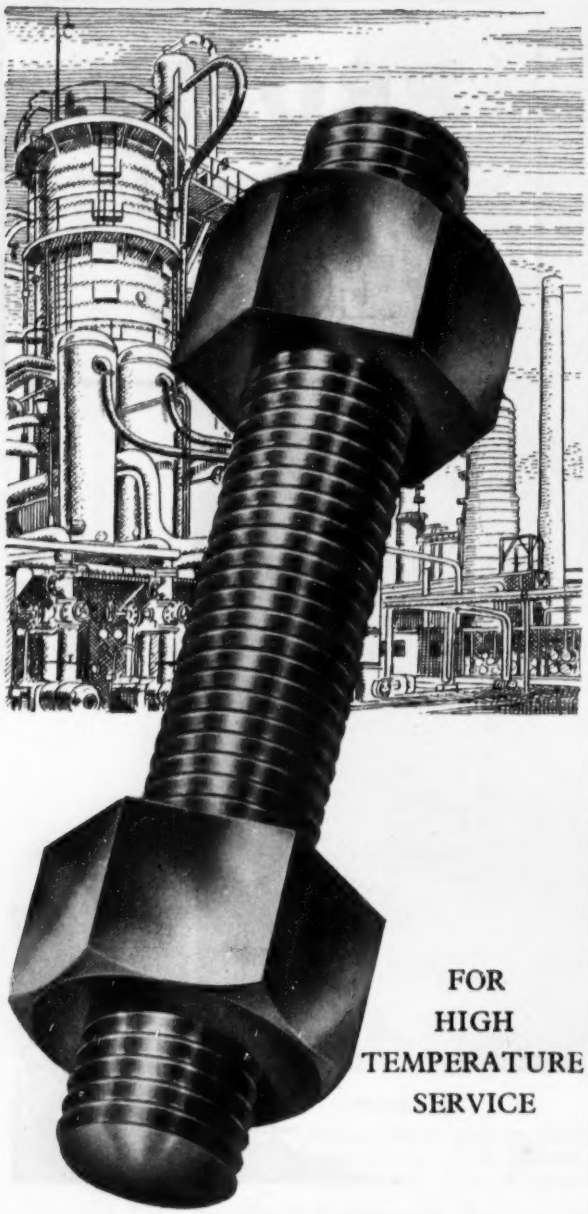

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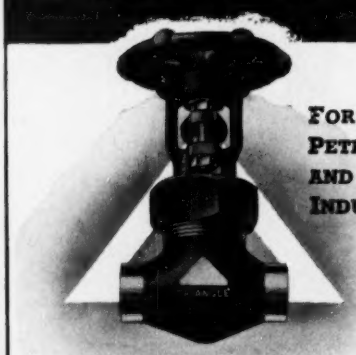

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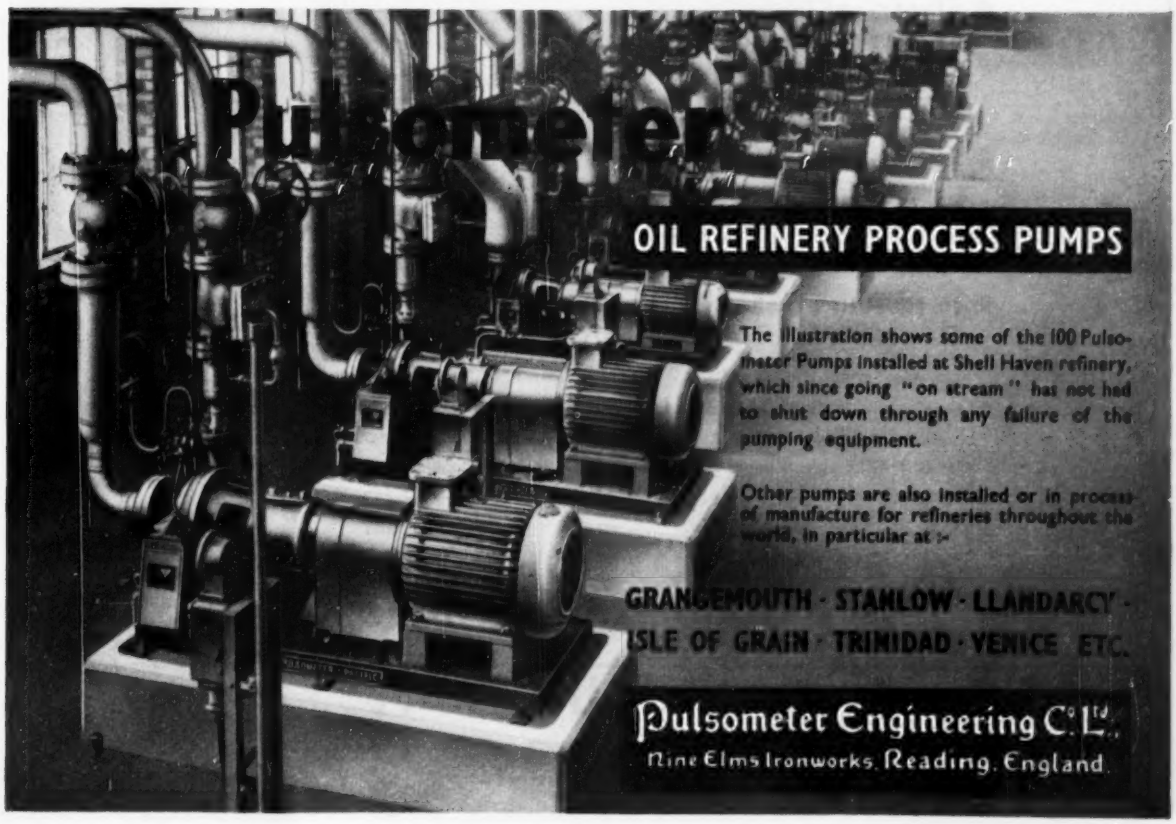
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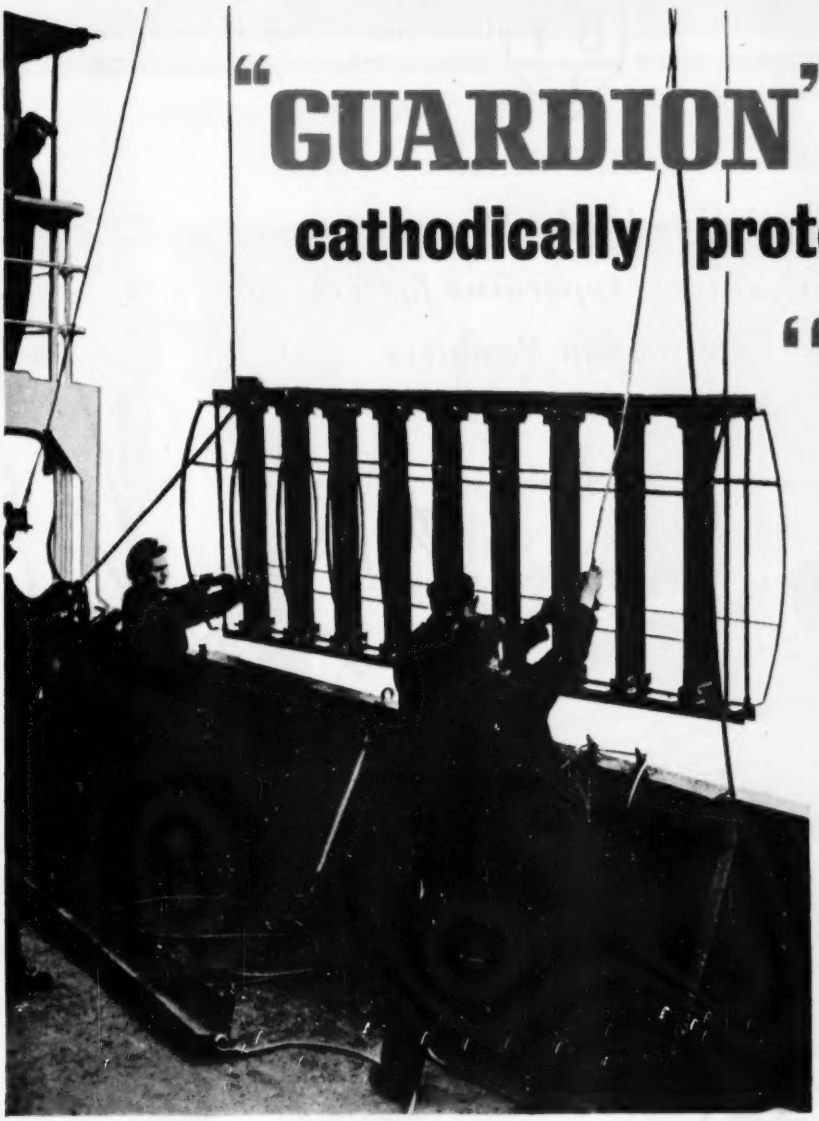

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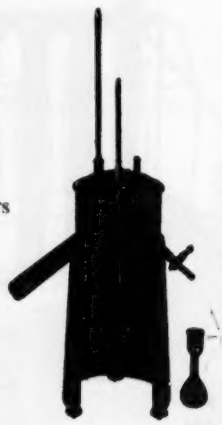

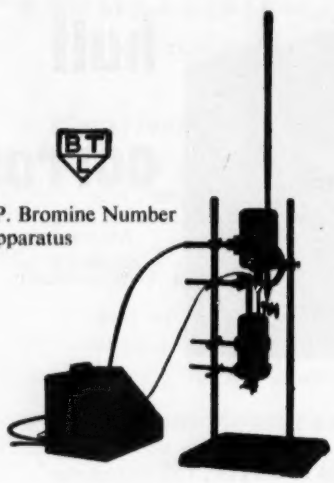

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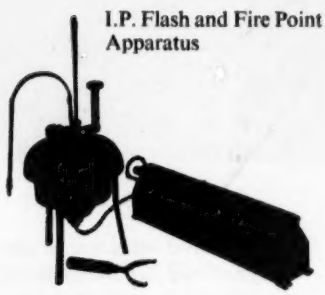

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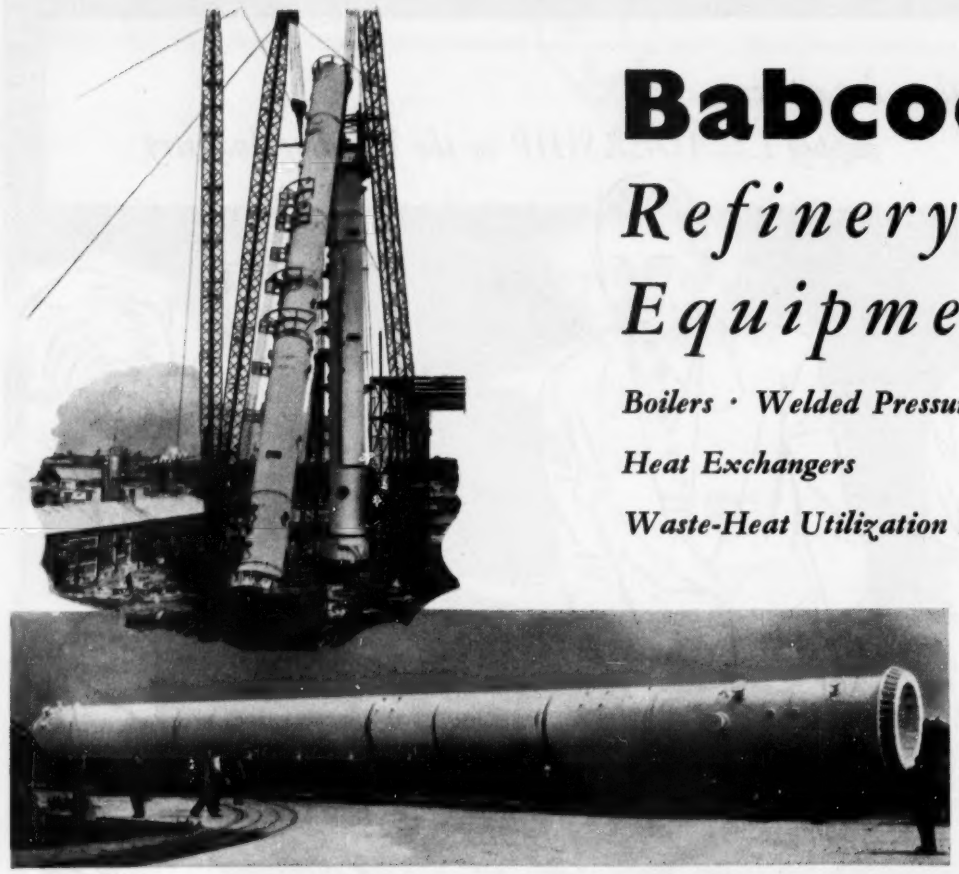

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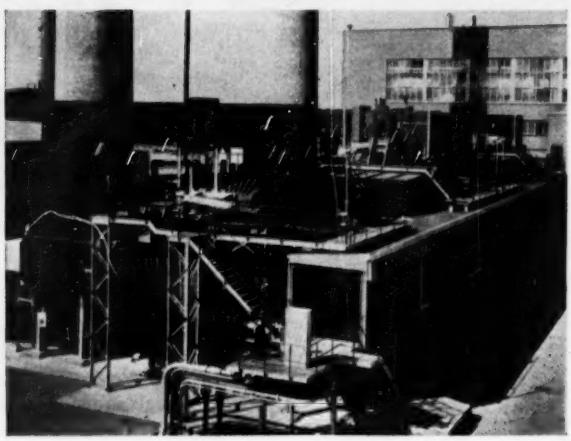

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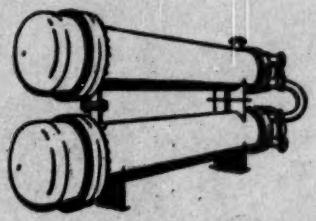

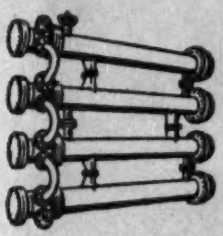

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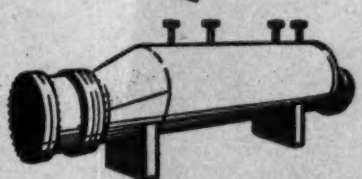

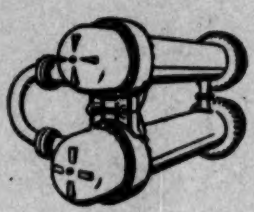

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